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PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES

PART 3. APPLICATIONS OF LIQUID CHROMATOGRAPHY

by

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PREFACE

This report is the third of a series resulting from a cooperative effort involving the Industrial Materials Research Institute (IMRI) of the National Research Council Canada (NRCC) (Boucherville, Québec) and Canadair Limited (Montréal, Québec). The subject is one of growing importance in high-technology manufacturing, namely the physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. This report describes the results of original research involving the application of various liquid chromatographic techniques to the graphite-epoxy system Narmco Rigidite 5208/WC3000. Other reports in the series include a general discussion and literature review, as well as studies of the application of other analytical techniques. The titles of the complete series are as follows:

Part 1. General Discussion and Literature Review
Part 2. Applications of Infrared Spectroscopy
Part 3. Applications of Liquid Chromatography
Part 4. Applications of Pyrolysis Gas Chromatography and Thermal Analysis
Part 5. A Study of the Room-Temperature Aging of Narmco 5208/WC3000 Prepreg
Part 6. Methods for Quality Control of Matrix Chemistry

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SUMMARY

The Narmco Rigidite 5208 epoxy resin system has been analysed by different liquid chromatography techniques, namely reverse-phase liquid chromatography (RPLC), high-speed reverse-phase liquid chromatography (HS-RPLC), and high-performance size-exclusion chromatography (HPSEC).

The best separation was obtained by reverse-phase liquid chromatography using conventional columns (25 cm long x 4.6 mm i.d.) packed with 5 µm particles. Epoxy resin was extracted from prepreg with tetrahydrofuran, and acetophenone was added as internal standard to quantify various peaks in the chromatogram. The separation was achieved on a nonpolar (octadecyl or octyl) bonded stationary phase with a water-acetonitrile gradient. The composition of acetonitrile in the mobile phase was increased linearly from 50% by volume to 100% in 15 minutes. Compounds eluting from the column were detected by UV absorption at 230 nm. The peak area or peak height was measured and normalized with respect to the acetophenone peak and the weight of the extracted epoxy resin. A reproducibility of less than 3% standard deviation was obtained for quantitative measurements of the main peaks. A smaller standard deviation was obtained with peak height than with peak area but the latter is recommended for definitive quantitative analysis since the results are less column-dependent and permit easier interlaboratory comparison.

The main peaks in the Narmco 5208 chromatogram have been identified by comparison of their retention times with those of individual components and by infrared spectroscopy of collected fractions.

Several batches of Narmco 5208 prepreg have been analysed by reverse-phase liquid chromatography and calibration curves have been established for the starting products (two epoxy resins and one hardener). The effect of heating on the prepreg has also been studied and this experiment has allowed the identification of the peak in the chromatogram corresponding to the initial reaction product between the main epoxy (TGDDM) and the hardener (DDS).

The main disadvantage of RPLC is the relatively long analysis time required for one injection. An analysis requires about 60 minutes including the regeneration time of the column. It has been shown that the use of a short column (4 cm long) packed with particles of 3 µm diameter allows a complete analysis in less than 10 minutes. This technique is called high-speed reverse-phase liquid chromatography to differentiate it from the previous one. The eluent composition during the gradient elution varied from

20% ACN/80% H_2O to 100% ACN in 3 minutes with a flow rate of the mobile phase maintained at 2.0 mL/min.

The resolution obtained with the short column is not as good as with a conventional column but it is acceptable and generally sufficient for a quality control laboratory. The possibility of using higher flow rates means that the analysis is completed in less time and that the solvent consumption is substantially decreased.

High-performance size-exclusion chromatography has been used to separate the epoxy resin on a molecular size basis. The use of particles of 5 μm diameter made with a highly crosslinked poly(styrene/divinylbenzene) copolymer allows efficient separation in less than 8 minutes. By comparison, conventional SEC columns require more than 40 minutes to achieve the same separation. However, this technique does not give as good resolution as reverse-phase liquid chromatography and, generally speaking, it seems less appropriate for evaluating the quality of an epoxy resin system.

RÉSUMÉ

Le système époxyde Narmco Rigidite 5208 a été analysé par différentes techniques de chromatographie liquide. Ces techniques sont la chromatographie liquide en phase inversée (CLPI), la chromatographie liquide en phase inversée à très haute vitesse (CLPI-HV), et la chromatographie d'exclusion haute performance (CEHP).

La meilleure séparation de la résine époxyde a été obtenue par chromatographie liquide haute performance en phase inversée sur des colonnes conventionelles (25 cm de longueur x 4.6 mm de diamètre interne) remplies avec des particules de 5 µm. La résine était extraite du préimprégné avec le solvant tétrahydrofuranne, et l'acétophénone était ajoutée comme standard interne pour quantifier les pics du chromatogramme. La séparation a été réalisée sur une phase stationnaire non-polaire (phase greffée octadécyle ou octyle) avec un gradient d'élution acétonitrile-eau. La teneur en acétonitrile dans la phase mobile augmentait linéairement de 50% (v/v) à 100% en 15 minutes. Les composés à la sortie de la colonne étaient détectés à 230 nm. Une excellente reproductibilité (écart type <3%) pour les mesures quantitatives des produits principaux a été obtenue en mesurant la surface ou la hauteur des pics et en normalisant celle-ci par rapport à l'acétophénone et au poids de la résine extraite. Un écart type plus faible a été obtenu en mesurant la hauteur du pic comparativement à la surface du pic. Cependant, l'utilisation de la surface est recommandée pour une analyse quantitative car les résultats sont alors indépendants de la colonne et permettent les comparaisons entre laboratoires.

Les principaux pics dans la résine Narmco 5208 ont été identifiés par comparaison de leurs temps de rétention avec les temps de rétention des produits individuels et par spectroscopie infrarouge des pics recueillis manuellement.

Différents lots de la résine Narmco 5208 ont été analysés et des courbes de calibration pour les produits de départ (deux résines et un durcisseur) ont été établies. L'effet du chauffage sur un prépreg a aussi été étudié et cela a permis de localiser sur le chromato - gramme le pic correspondant au produit de réaction principal entre une molécule de l'époxyde majeur (TGDDM) et une molécule du durcisseur (DDS).

L'inconvénient majeur de la chromatographie liquide en phase inversée est la longueur du temps d'analyse nécessaire par injection. En incluant le temps de regénération de la colonne, une analyse nécessite environ 60 minutes. L'utilisation d'une courte colonne de 4 cm de longueur remplie avec des particules de 3 µm de diamètre a permis de réaliser une analyse complète en moins de 10 minutes. Cette technique s'appelle la chromatographie liquide en phase inversée à très haute vitesse pour la distinguer de la précédente. Le

gradient d'élution variait de 20% ACN/80% H_2O à 100% ACN en 3 minutes avec un débit de la phase mobile de 2.0 mL/min.

La résolution obtenue avec cette colonne n'est pas aussi bonne qu'avec une colonne conventionnelle mais elle est acceptable et généralement suffisante pour un laboratoire de contrôle de qualité. La possibilité d'utiliser un débit d'éluant élevé signifie qu'une analyse est terminée en moins de temps et que la consommation de solvant diminue substantiellement.

La chromatographie d'exclusion haute performance a permis la séparation de la résine époxyde sur la base des grandeurs moléculaires. L'utilisation de nouvelles particules de 5 µm de diamètre fabriquée avec un copolymère polystyrène divinylbenzène hautement réticulé permet d'obtenir une séparation très efficace en moins de 8 minutes. Par comparaison, les colonnes conventionnelles en chromatographie d'exclusion nécessitent plus de 40 minutes pour réaliser la même séparation. Cependant, cette technique ne donne pas une aussi bonne résolution que la chromatographie liquide en phase inversée et elle semble moins appropriée pour évaluer la qualité d'une résine époxyde.

1. INTRODUCTION

Liquid chromatography (LC) is an excellent technique for detecting small variations in the chemical composition of an epoxy resin system. The separation of a complex mixture into individual components makes it possible to monitor precisely the overall composition, including the extent of reaction advancement between an epoxy resin and a hardener. Government regulatory agencies have recommended liquid chromatography and infrared spectroscopy as analytical techniques to be used for quality control of prepreg used in the fabrication of primary structures of an aircraft.

Part 1 of this work [1] gives a general description of organic-matrix composites and useful analytical methods for studying the matrix chemistry, together with a literature review on the chemical behaviour of some epoxy resin systems. The aims of the cooperative work done with Canadair Ltd. on composites included the development of specific analytical methods to characterize epoxy-graphite systems. This development was done with the Narmco Rigidite 5208 system which is described in detail in Part 1. Briefly, the resin consists of three main components. The major epoxy (about 67% by weight) is a complex mixture of about 60% tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and 40% higher oligomers and by-products. The second component (about 10% by weight) is the minor epoxy, a bisphenol A Novolac epoxy. Finally, the third component is 4,4'-diaminodiphenylsulphone (DDS) acting as a hardener (about 23% by weight).

Infrared spectroscopy methods developed for the Narmco 5208 system are given in Part 2 of this work [2]. In the present report (Part 3), experimental results pertaining to the development of liquid chromatography methods will be described.

Liquid chromatography can be divided into different classes. In this work, three different techniques were studied. The first is reverse-phase liquid chromatography (RPLC). The second, high-speed reverse-phase liquid chromatography (HS-RPLC), is a variant of the first one, and the third technique is high-performance size-exclusion chromatography (HPSEC).

In reverse-phase liquid chromatography, conventional columns (15-35 cm long x 4.0-4.6 mm i.d.) packed with particles of 5 or 10 μm diameter were used with a typical eluent flow rate of 1.0 mL/min. The main purpose of this work was the optimization of an LC method to accurately analyse the extract of an epoxy resin prepreg.

The method involving high-speed reverse-phase liquid chromatography demonstrates the application of short columns (4 cm long) packed with small particles of 3 μm diameter. With these columns, the flow rate of the mobile phase can be increased to 2.0 or 3.0

mL/min without a significant decrease of the column efficiency. Thus, the analysis time is considerably shorter than with conventional LC columns.

In both these cases, the separation is governed largely by the polarity of the compound in relation to the eluent polarity. A separation technique based on the molecular size of the solute was also examined, and a good separation of the epoxy system was achieved using a single SEC column. This method can be used with a conventional liquid chromatograph and allows faster analysis than do standard SEC methods.

Finally, in the last chapter, recommended LC methods for the analysis of epoxy resin prepregs are summarized.

2. EXPERIMENTAL SECTION

2.1 Materials

The composite system chosen for intensive study was the Rigidite 5208/WC3000 system manufactured by Narmco Materials, Inc. The reinforcement consists of Celion graphite fibres, 3000 fibres per yarn, woven in an 8-harness satin pattern (each warp yarn passing alternately over seven fill yarns and under one fill yarn). The woven fabric is impregnated with Rigidite 5208 resin to a nominal resin content of 42% by weight and the prepreg is supplied on a plastic sheet in rolls. The resin is commonly referred to as simply "Narmco 5208". The following samples of Rigidite 5208/WC3000 prepreg or Rigidite 5208 neat resin were obtained from Canadair Ltd:

Prepreg, Batch Number 1010
Prepreg, Batch Number 1014
Prepreg, Batch Number 1101
Prepreg, Batch Number 1103
Prepreg, Batch Number 1104
Neat resin on plastic backing sheet, Batch Number 1047
Neat resin in bulk form, Batch Number 1023.

Prepreg and reactive resin samples were stored in a freezer at all times except for sampling and performance of experiments. Samples of the following components were obtained from the respective companies:

Ciba-Geigy Araldite MY 720 epoxy resin (TGDDM), Lot Y5085
Ciba-Geigy Hardener HT 976 (DDS), Lot IL2096
Celanese Epi-Rez SU-8 (bisphenol A Novolac epoxy), Lot L11-82182.

These were stored in a refrigerator.

2.2 Instrumentation

For RPLC, the chromatographic system consisted of a Varian Model 5000 liquid chromatograph (Varian Instrument Group) with an automatic universal injector (10 μL), Model 7126 from Rheodyne Inc. For HS-RPLC, an automatic loop injector (1 μL loop), Model 7410 from Rheodyne, was used. The detector was a Varian variable wavelength detector Model UV-100 with a 4.5 μL flow cell. Chromatograms were recorded on a

Varian Vista 401 data station and data were transferred to an Apple II+ computer via an RS-232 interface to perform additional data processing.

The size-exclusion chromatographic system consisted of a Perkin-Elmer Series 3B liquid chromatograph with a manual universal Rheodyne injector (10 µL loop) Model 7125. The detector was either a water-thermostatted Varian refractive index detector Model RI–3 or a Varian variable wavelength UV detector Model UV-100.

2.3 Columns

The columns were purchased pre-packed. For RPLC, the following were used: MCH-5-n-CAP, 15 cm long x 4.0 mm i.d., 5 µm particles (Varian); MCH-5-n-CAP, 30 cm long x 4.0 mm i.d., 10 µm particles (Varian); MCH-10, 30 cm long x 4.0 mm i.d., 10 µm particles (Varian); CH-10, 30 cm long x 4.0 mm i.d., 10 µm particles (Varian); Hypersil MOS-1, 25 cm long x 4.6 mm i.d., 5 µm particles (Chromatography Sciences Company); Hypersil ODS, 25 cm long x 4.6 mm i.d., 5 µm particles (Chromatography Sciences Company); Partisil ODS-3, 25 cm long x 4.6 mm i.d., 10 µm particles (Whatman); Partisil ODS-2, 25 cm long x 4.6 mm i.d., 10 µm particles (Whatman); PRP–1, 25 cm long x 4.1 mm i.d, 10 µm particles (Hamilton).

For HS-RPLC, a Varian Ultra-fast C_{18}-3, 4.0 cm long x 4.6 mm i.d., 3 µm particles, was used.

The HPSEC column was a PLgel column, 30 cm long x 7.5 mm i.d., 5 µm particles, from Polymer Laboratories.

3. REVERSE-PHASE LIQUID CHROMATOGRAPHY

3.1 Introduction

Reverse-phase liquid chromatography (RPLC) is currently used in about 80-90% of all the separations done by high-performance liquid chromatography (HPLC) [3]. The popularity of this technique is due to many factors. To be specific, the excellent reproducibility of separations, the good stability of stationary phases, the versatility in terms of classes of chemical compounds which can be separated efficiently, and the ease of obtaining reproducible gradient elution are the principal reasons cited by analytical chemists.

As opposed to normal-phase liquid chromatography (NPLC), reverse-phase liquid chromatography makes use of a nonpolar stationary phase with a polar mobile phase or eluent. Usually, the stationary phase is a hydrocarbonaceous bonded phase, the most common bonded groups being octyl (C8) and octadecyl (C18) alkyl chains. These groups are bonded to silica particles to convert polar hydroxyl groups to a nonpolar surface. The eluent generally consists of a binary mixture of water with an organic solvent such as acetonitrile (ACN), methanol (MeOH), or tetrahydrofuran (THF). To a first approximation, the retention mechanism of a solute is governed by its polarity in relation to the polarity of the mobile phase. A nonpolar compound is more strongly retained on a nonpolar stationary phase than is a polar compound. Thus, an increase of the organic content of the eluent decreases the polarity of the mobile phase and results in more rapid elution of the solute. Consequently, for a given chromatographic column, a method of separation is optimized by varying the eluent composition in order to obtain the most efficient separation in the shortest time.

In isocratic elution, the eluent composition is not modified during a chromatographic run. In gradient elution, on the other hand, usually the percentage of organic solvent in the mobile phase is gradually increased in order to increase the eluotropic strength and speed up the elution of strongly retained compounds. The main advantage of this technique is that the more rapidly-eluting compounds can be well separated by using a more polar mobile phase at the beginning, and then the more strongly retained compounds can be eluted in a reasonable time by continuously increasing the eluotropic strength of the eluent. Among the disadvantages are the fact that the column must be regenerated to its initial condition after each analysis (a time-consuming procedure), and the detector must be insensitive to the variation of the mobile phase composition. For the analysis of epoxy

resins, which contain many compounds with different polarities, gradient elution must be used to achieve an efficient separation.

3.2 Solvent for extraction of the resin

The choice of a solvent for extraction of the resin from Narmco 5208 prepreg has been discussed in Part 2 [2]. Among the tested solvents, tetrahydrofuran (THF) was the best in terms of resin solubility, so it was selected to perform the extraction for liquid chromatography work. Scanning electron microscope (SEM) photographs have shown that the organic resin is completely removed by the THF [4]. The extraction was performed at room temperature on a piece of prepreg of 5 cm x 5 cm in three stages (about 15 minutes each) using 50 mL, 30 mL, and 20 mL of tetrahydrofuran. The resin concentration in the resulting solution was about 6 mg/mL. The exact weight of resin extracted was determined by recovering, drying, and weighing the graphite fibres, and subtracting the weight from the initial prepreg weight. All extracts were filtered through a Millex-SR 0.5 μm filter unit (Millipore Corporation) before injection on the chromatographic column.

3.3 Optimization of the separation of Narmco 5208 resin

3.3.1 Preliminary trials

The initial separation of the epoxy system was done according to the method proposed by Hinrichs and Thuen [5] of Narmco Materials Inc. A sample volume of 10 μL of the extract was injected on an MCH–10 column, 30 cm long x 4 mm i.d., made by Varian. The stationary phase was an octadecyl bonded silica phase with particles of 10 μm diameter. The detector was a Varian UV detector set at 230 nm. The linear water-acetonitrile gradient is given in Table 1. The flow rate was maintained constant at 1.0 mL/min and the column was kept at 25°C.

Figure 1 shows the chromatogram of the epoxy prepreg extract obtained using these conditions. From comparison with the literature, it can be assumed that peak #1 is due to the hardener DDS and peak #4 to the main epoxy TGDDM. In order to find the product of the reaction between these two molecules, a sample of prepreg was heated for one hour at 120°C before extraction with tetrahydrofuran. The weight extracted was the same as for the unheated sample (41.2%). It was found that heating causes a significant increase in the

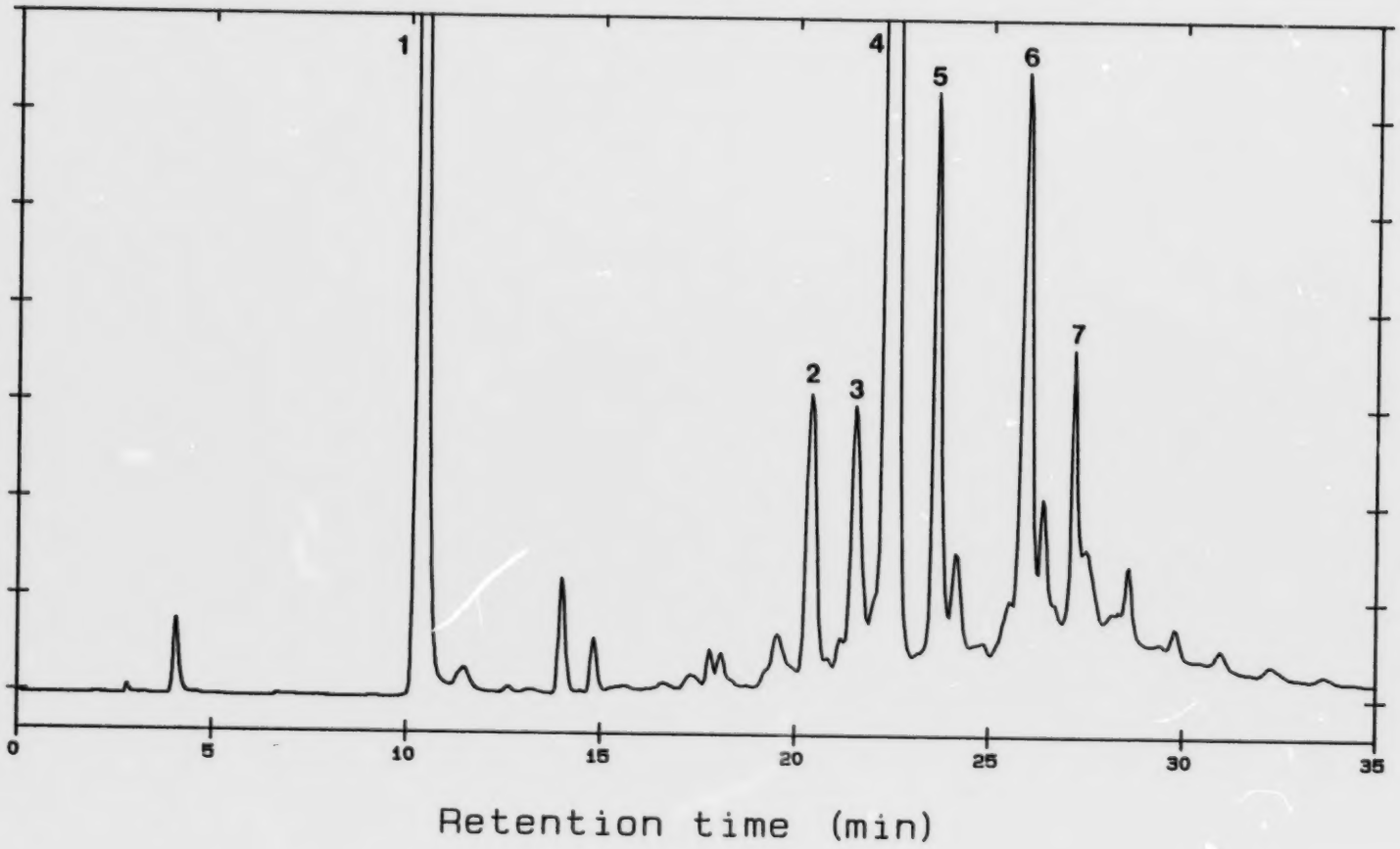
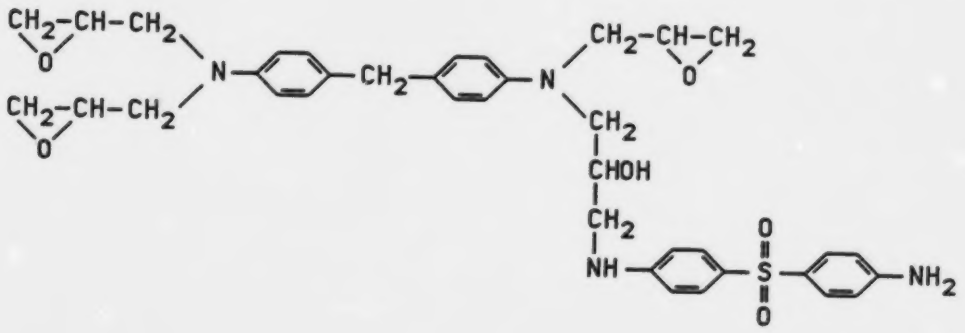


Figure 1: RPLC separation of the THF extract of Narmco 5208 prepreg, batch #1103, using the gradient elution method of Hinrichs and Thuen.
Column: MCH-10, 30 cm X 4.0 mm i.d..

Table 1. Water-acetonitrile gradient reported by Hinrichs and Thuen [5].

Time (min)	Eluent composition (H_2O/ACN, % by volume)
0-20	76/24 to 18/82
20-21	18/82 to 1/99
21-36	1/99 (constant)
36-39	1/99 to 76/24
39-55	76/24 (constant)

intensity of peak #2, relative to the others. This peak is therefore probably due to the initial reaction product of TGDDM and DDS:



However, the separation is not fully optimized and the analysis time is relatively long. An elution time of 10 minutes is necessary before the detection of the DDS (peak #1). Moreover, as almost all the peaks are eluted between 20 and 30 minutes, there is a strong possibility of overlapped or unresolved peaks. In order to optimize the separation, the elution of the first peaks must be accelerated and the resolution of the later peaks must be improved. Hence the chromatographic conditions were studied more thoroughly so as to optimize the separation of the resin system.

3.3.2 Mobile phase composition

A number of different mobile phase compositions were tried using a Varian MCH–5–n–CAP column, 30 cm long x 4.0 mm i.d.. The same column was used for all

the tests in order to eliminate any possible variations due to a change of column. Peak detection was done at 230 nm. The sample was a THF extract of Narmco 5208 prepreg, batch #1103.

Several isocratic H_2O/ACN eluents were tested but the separations were always unacceptable. If the organic content of the mobile phase is too high, the first peaks are not resolved; conversely, if the percentage of water is too high, some compounds are not eluted from the column. To date, it seems that gradient elution is the best way to achieve an efficient separation in a reasonable time. However, some computer methods have been published recently which make it possible to develop a multi-component isocratic solvent based on the results of gradient elutions using simpler mixtures. It would be interesting to pursue the development of such methods in the future.

Different gradients were tried in order to optimize the separation. Various mixtures of ACN/H_2O, THF/H_2O, MeOH/H_2O and ACN/THF/H_2O were tested and the best results were obtained with the linear gradient described in Table 2. The flow rate was maintained constant at 1.0 mL/min during the chromatographic run and the temperature of the column was kept at 25°C.

Table 2. Optimum gradient for the RPLC separation of Narmco 5208 epoxy resin.

Time (min)	Eluent composition (H_2O/ACN, % by volume)
0 - 15	50/50 to 0/100
15 - 30	0/100 (constant)
30 - 31	0/100 to 50/50
31 - 50	50/50 (constant)

Figure 2 shows the chromatogram obtained using this gradient. Figure 2a represents it on the same scale as Figure 1, whereas Figure 2b shows it on a less-expanded scale in order to show all the peaks completely and allow comparison of their intensities. All subsequent chromatograms will be shown using an expanded scale (as in Figures 1 and 2a) in order to make it easier to see the smaller peaks. In Figure 2, the peaks are more evenly distributed than in Figure 1 and the overall time required is shorter. Acetonitrile is preferable to tetrahydrofuran as eluent because its UV cutoff is at 190 nm compared to 215

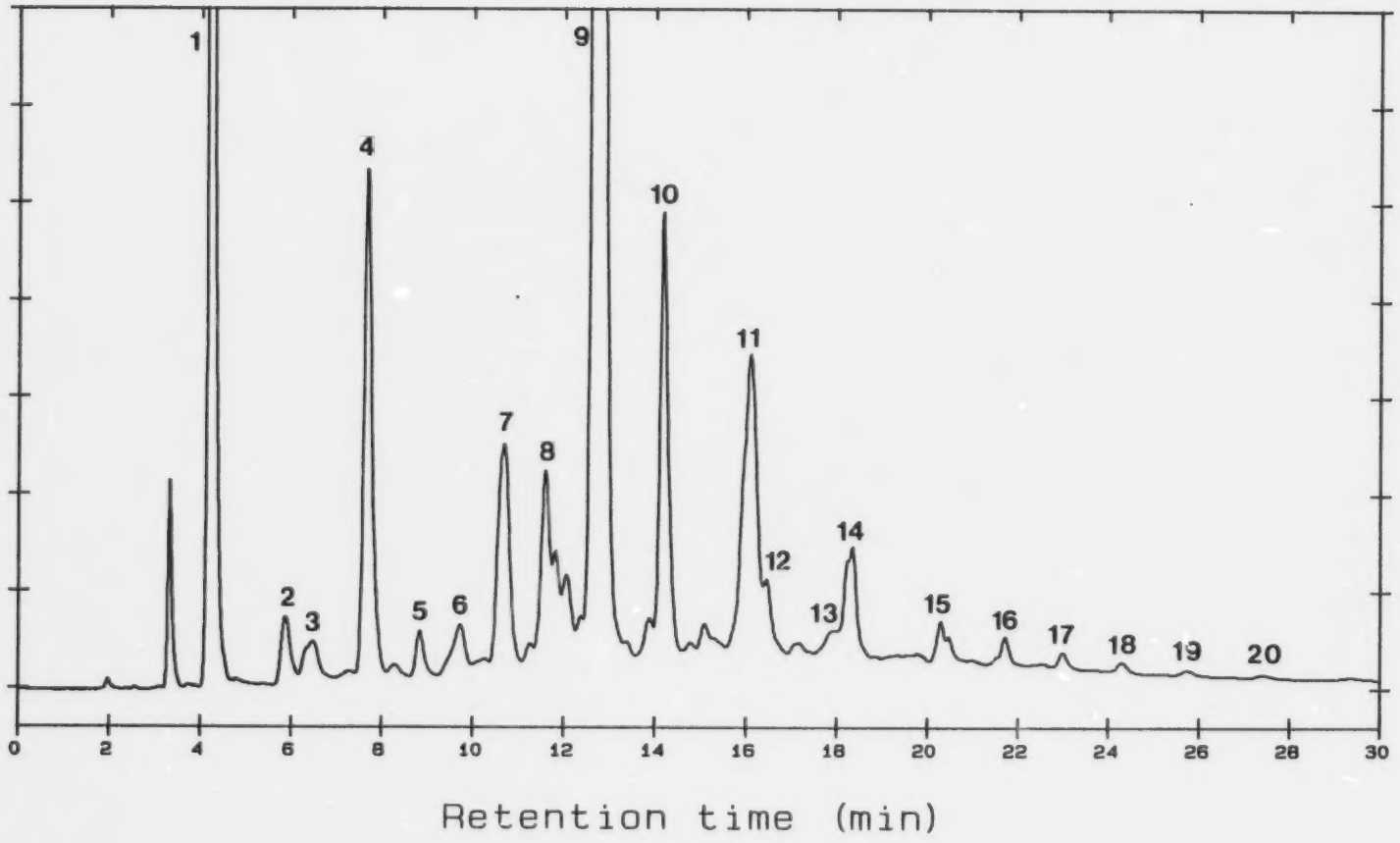


Figure 2a: RPLC separation of the THF extract of Narmco 5208 prepreg, batch #1103, using the gradient elution method described in Table 2.
Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d..
Expanded scale.

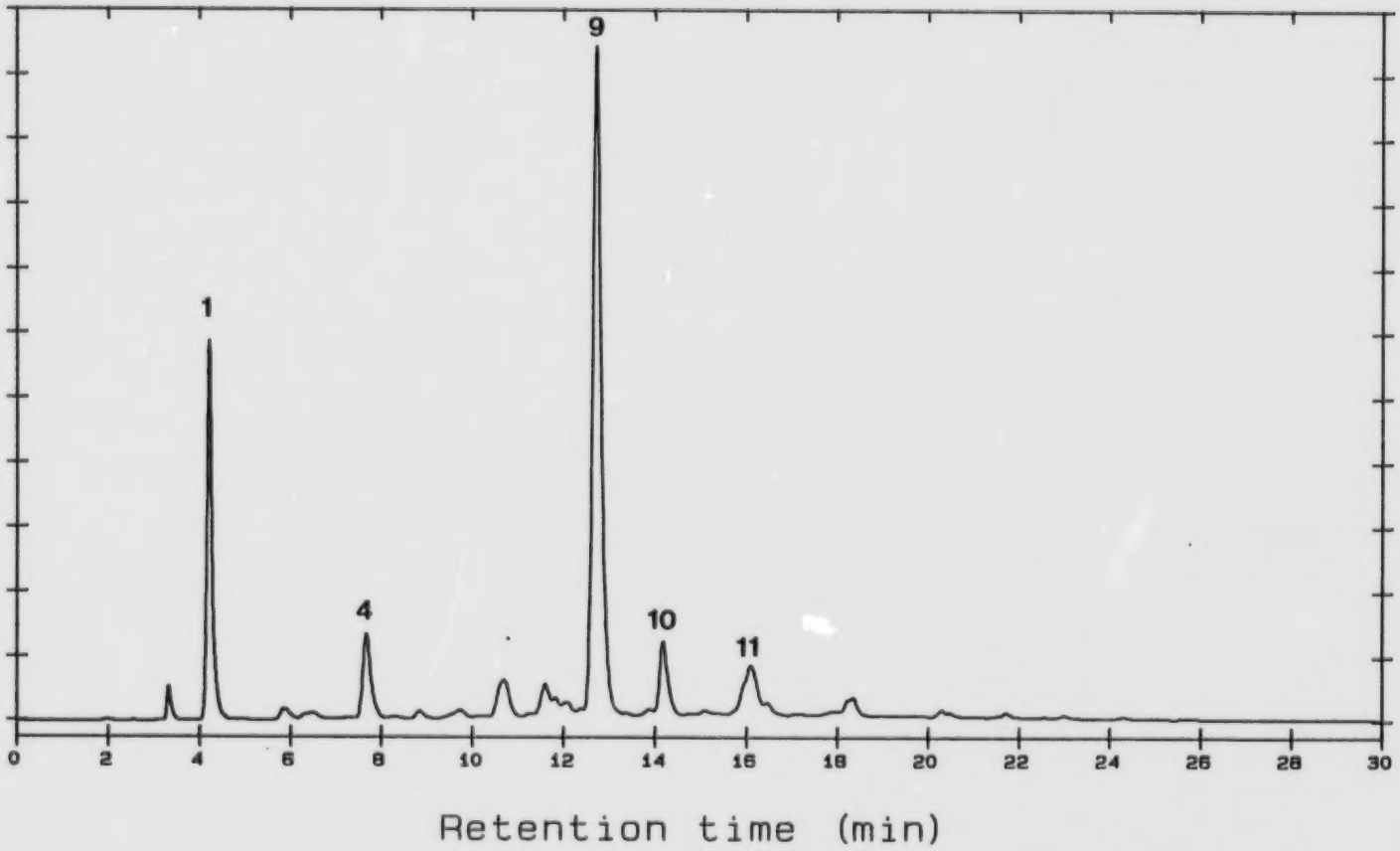


Figure 2b: RPLC separation of the THF extract of Narmco 5208 prepreg, batch #1103, using the gradient elution method described in Table 2.
Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d..
Normal scale.

nm for THF. Thus, no baseline drift is observed with an ACN/H_2O gradient, which was not the case with THF [6]. Identification of the peaks will be discussed in Section 3.4.

3.3.3 Chromatographic column

The efficiency of 10 different columns for the separation of Narmco 5208 resin was evaluated using the gradient elution method described in the previous section. Table 3 lists these columns with their particular characteristics. New columns were used to do this comparison in order to eliminate possible effects due to column degradation. The same batch of prepreg (#1103) was used throughout.

Table 3. Characteristics of various RPLC columns.

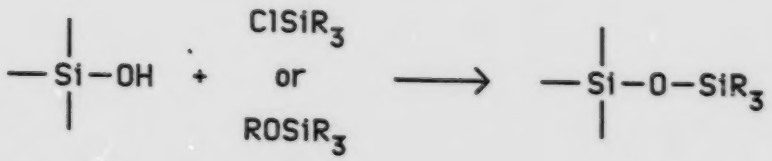
No.	Name	Particle diameter (μm)	Length (cm)	Internal diameter (mm)	Manufacturer
1	Hypersil ODS	5	25	4.6	CSC
2	Hypersil MOS-1	5	25	4.6	CSC
3	CH-10	10	30	4.0	Varian
4	MCH-10	10	30	4.0	Varian
5	MCH-10-n-CAP	10	30	4.0	Varian
6	MCH-5-n-CAP	5	30	4.0	Varian
7	MCH-5-n-CAP	5	15	4.0	Varian
8	Partisil ODS-3	10	25	4.6	Whatman
9	Partisil ODS-2	10	25	4.6	Whatman
10	PRP-1	10	25	4.1	Hamilton

No.	Name	Alkyl chain	Particle shape	Surface layer	Secondary capping
1	Hypersil ODS	C18	Spherical	Monomeric	Yes
2	Hypersil MOS-1	C8	Spherical	Monomeric	Yes
3	CH-10	C18	Irregular	Polymeric	No
4	MCH-10	C18	Irregular	Monomeric	No
5	MCH-10-n-CAP	C18	Irregular	Monomeric	Yes
6	MCH-5-n-CAP	C18	Irregular	Monomeric	Yes
7	MCH-5-n-CAP	C18	Irregular	Monomeric	Yes
8	Partisil ODS-3	C18	Irregular	Monomeric	Yes
9	Partisil ODS-2	C18	Irregular	Polymeric	No
10	PRP-1	----	Spherical	----	----

Figures 2 to 11 show the chromatograms obtained with these columns. The best separation was achieved with the Hypersil MOS–1 column (Figure 3). The resolution is excellent for the separation of an epoxy resin system. The second best choice is the MCH–5–n–CAP (30 cm long) column (Figure 2). The Hypersil MOS–1 column was obtained only recently, so the MCH-5-n-CAP column was used to perform the majority of the analyses in this work. With the MCH-5-n-CAP column, the main peaks are well separated but the resolution of smaller peaks is slightly better on the Hypersil MOS–1 column and the analysis time is shorter. It is interesting to note that more oligomers can be detected with the Hypersil MOS-1 column (small peaks at the end of the chromatogram, after 17 minutes in Figure 3).

Bonded-phase particles are made from silica particles, which can have spherical or irregular shapes. Spherical particles allow a higher permeability and thus require a lower solvent pressure. They are more costly to produce but they give more stable and regular packing. Irregular particles have a higher surface area which can lead to a higher column efficiency if the packing of the column is well done. It seems that both particle shapes can give similar performance in terms of column efficiency. Columns #1, #2, and #10 have spherical particles and the others have irregular particles. The current trend is towards the use of spherical particles because they are easier to pack and they improve the column stability.

The base silica gel has about 8 SiOH (silanol) groups per square nanometer. The silanization procedure involves the bonding of an organochlorosilane or organoalkoxy - silane reagent to form siloxanes:



Siloxanes are stable from pH 2.0 to about 8.5. Depending on the silanization conditions, it is possible to obtain a monomeric or a polymeric layer. The selectivity of a stationary phase for nonpolar compounds is slightly increased with a polymeric layer, and the sample capacity is superior to that of a monomeric layer. However, if the polymeric layer is too thick, the mass transfer resistance can decrease the column efficiency. In general, mono - layer coverage will give better efficiency than polymeric layers with high coverage.

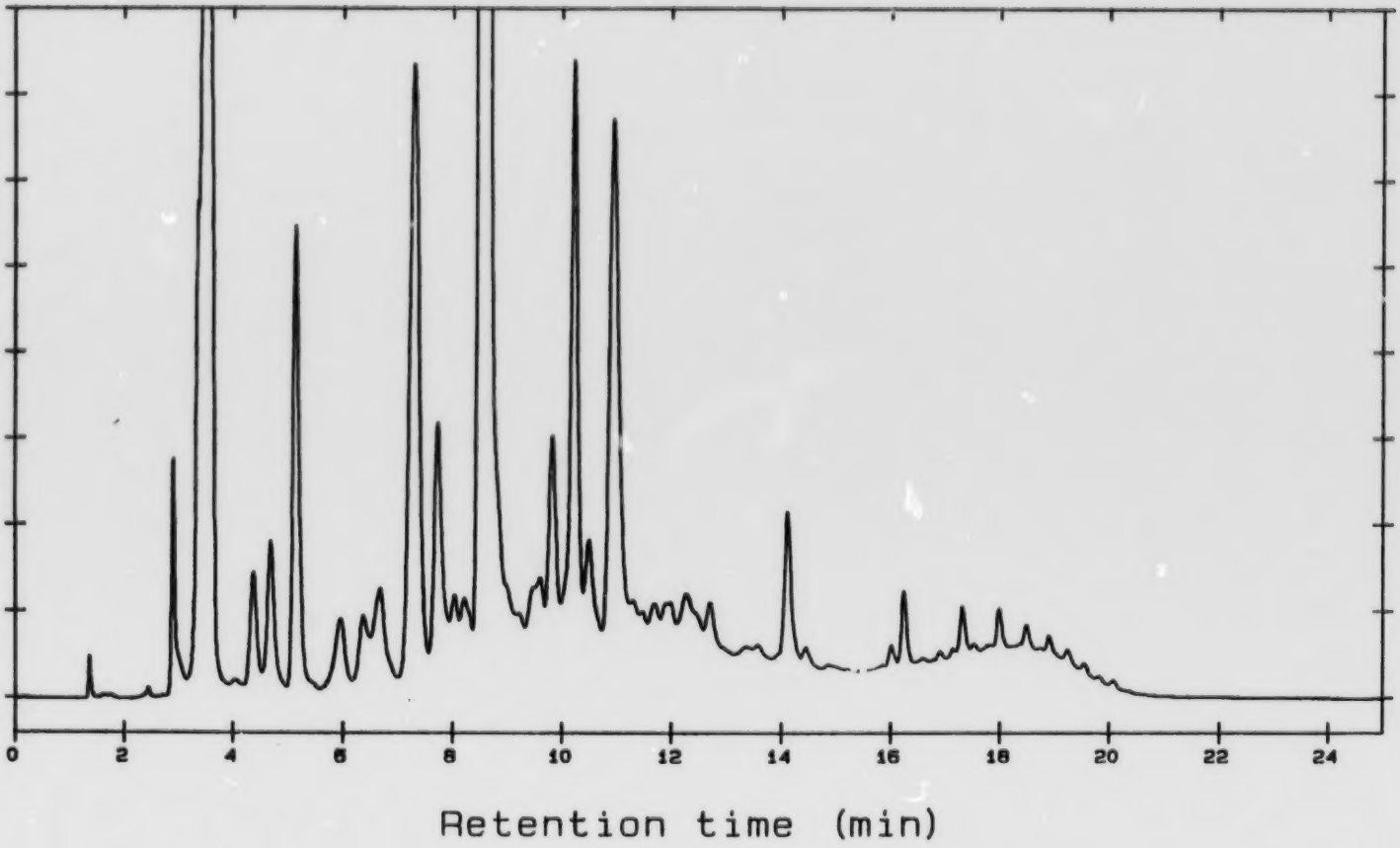


Figure 3: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103.
Column: Hypersil MOS-1, 25 cm X 4.6 mm i.d..

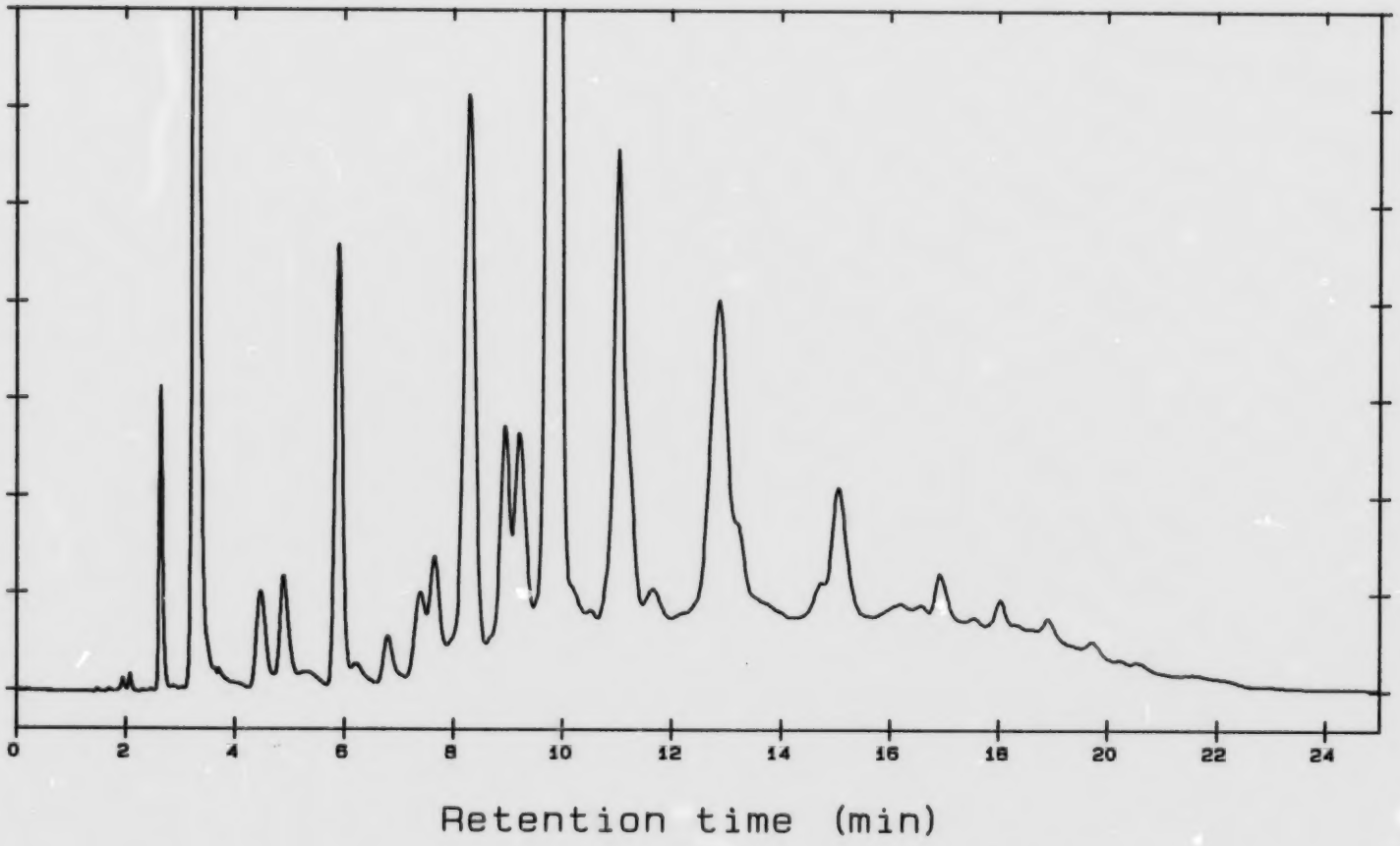


Figure 4: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103.
Column: MCH-10-n-CAP, 30 cm X 4.0 mm i.d..

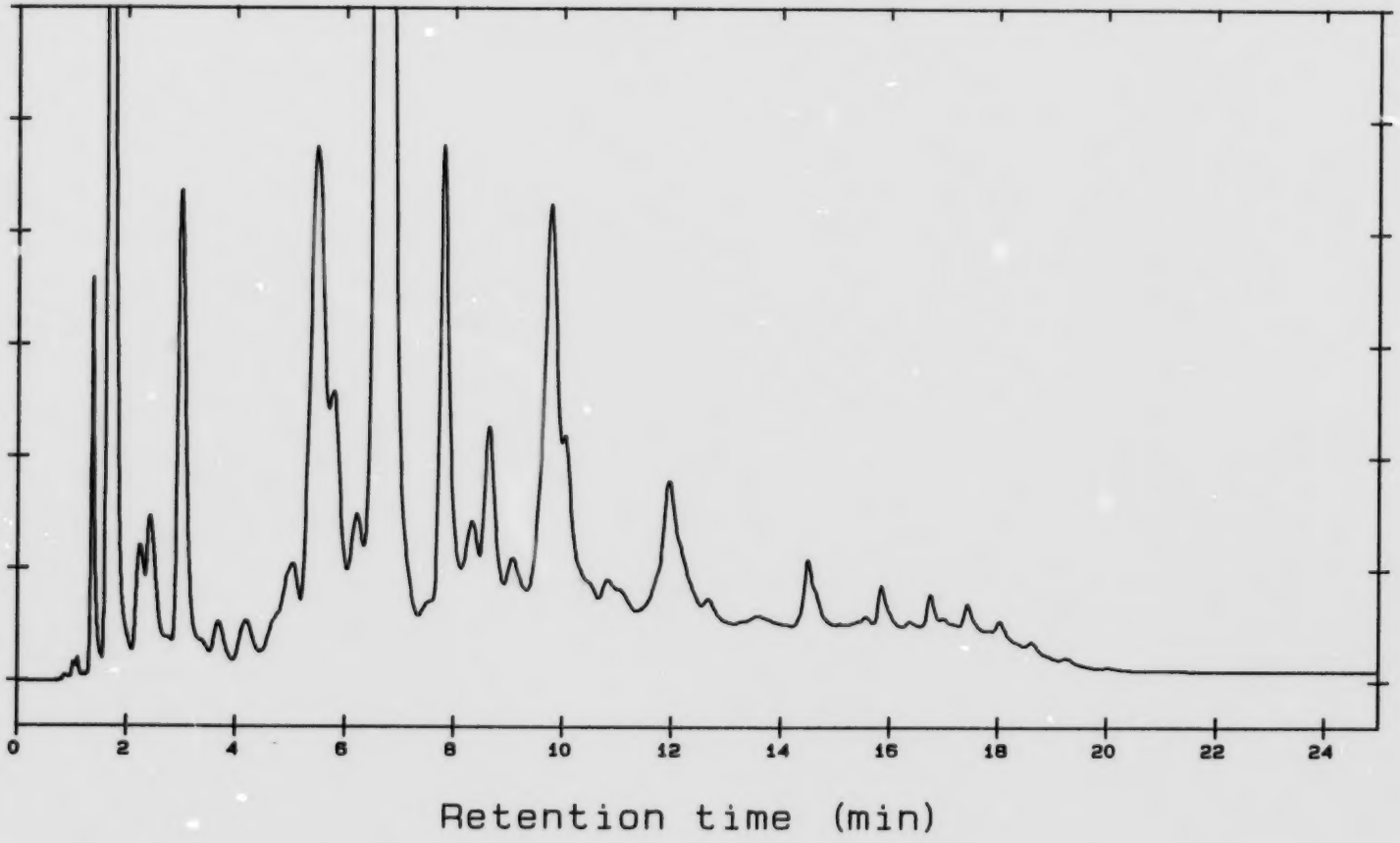


Figure 5: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: MCH-5-n-CAP, 15 cm X 4.0 mm i.d..

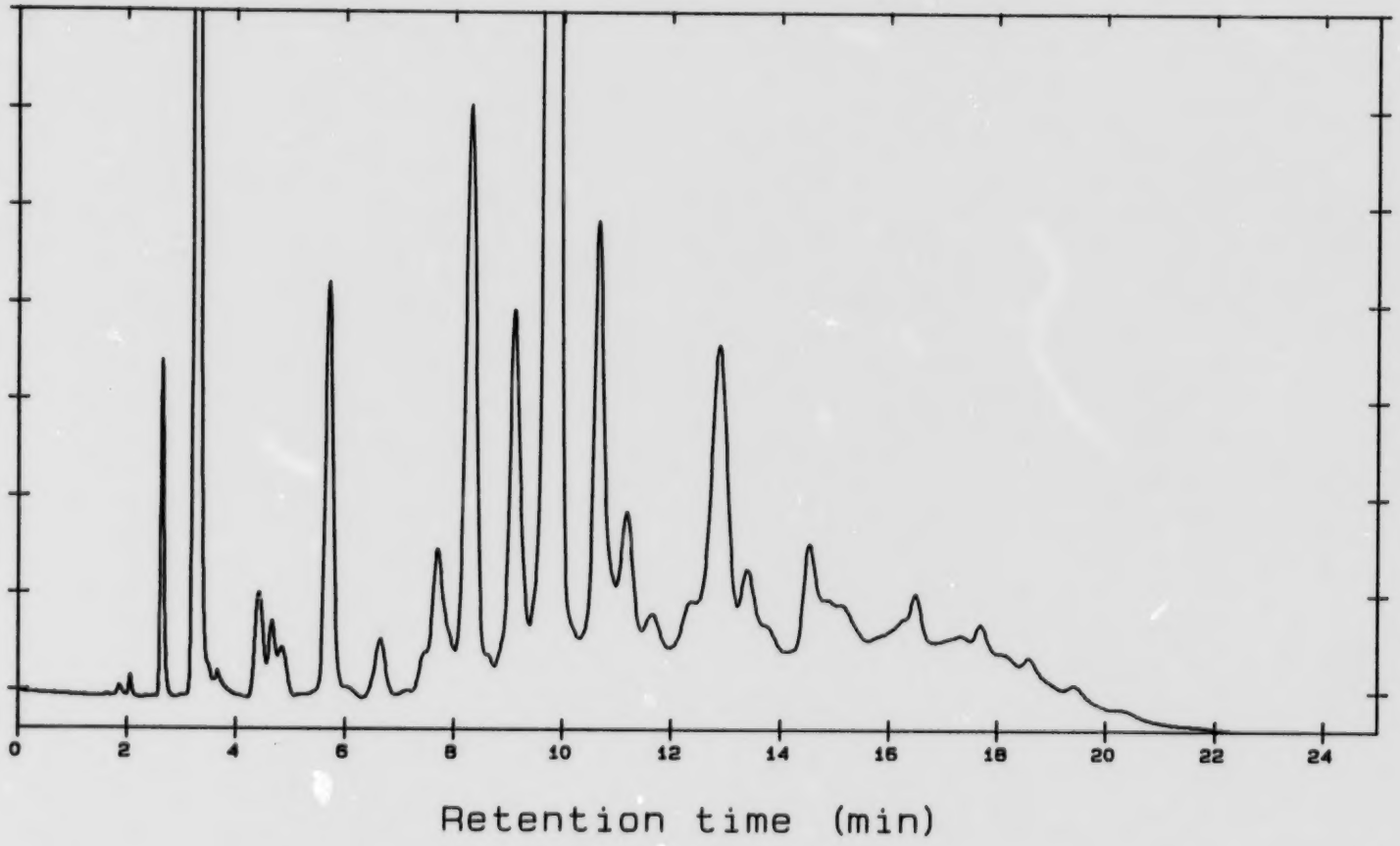


Figure 6: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: MCH-10, 30 cm X 4.0 mm i.d..

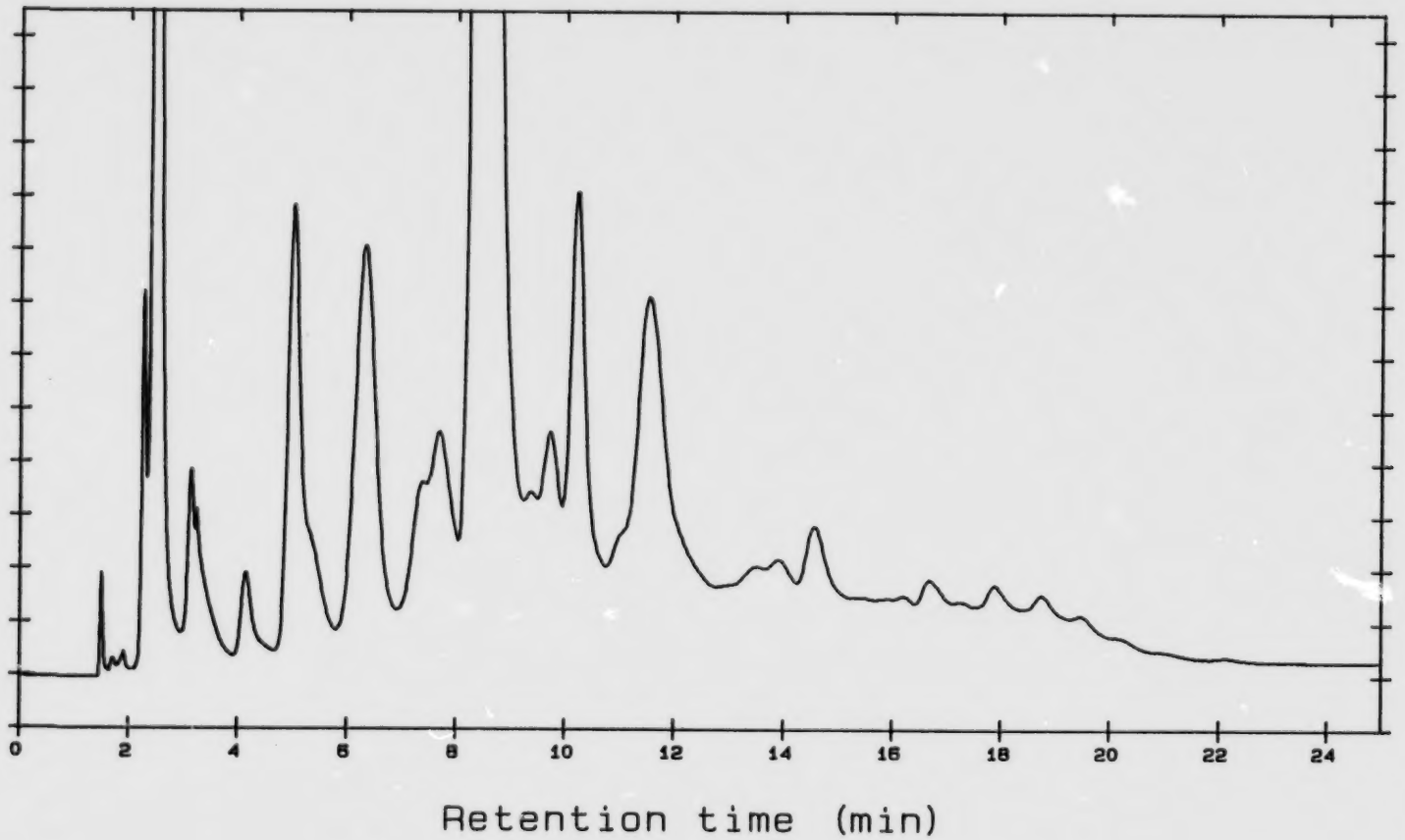


Figure 7: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: CH-10, 30 cm X 4.0 mm i.d..

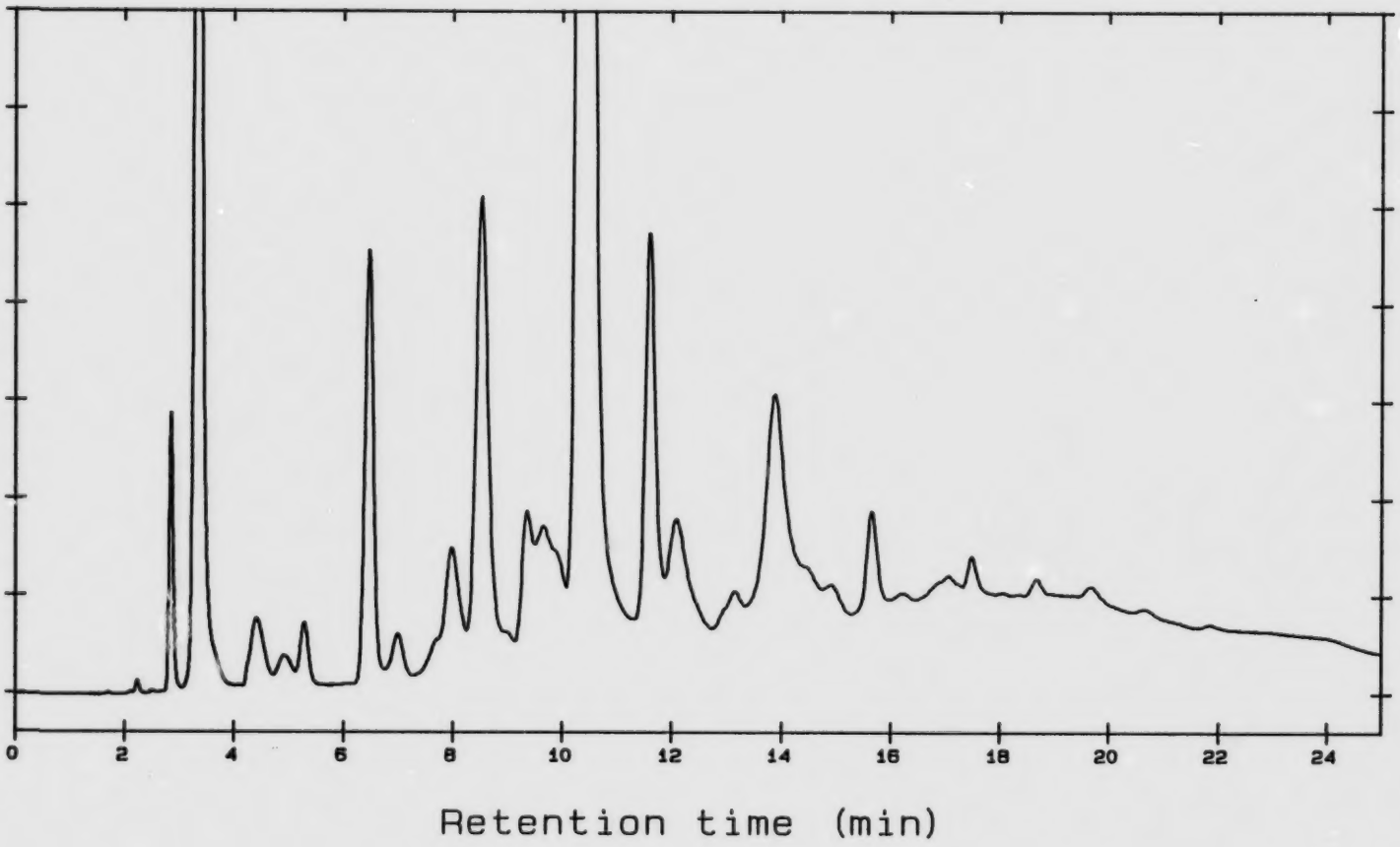


Figure 8: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Partisil ODS-2, 25 cm X 4.6 mm i.d..

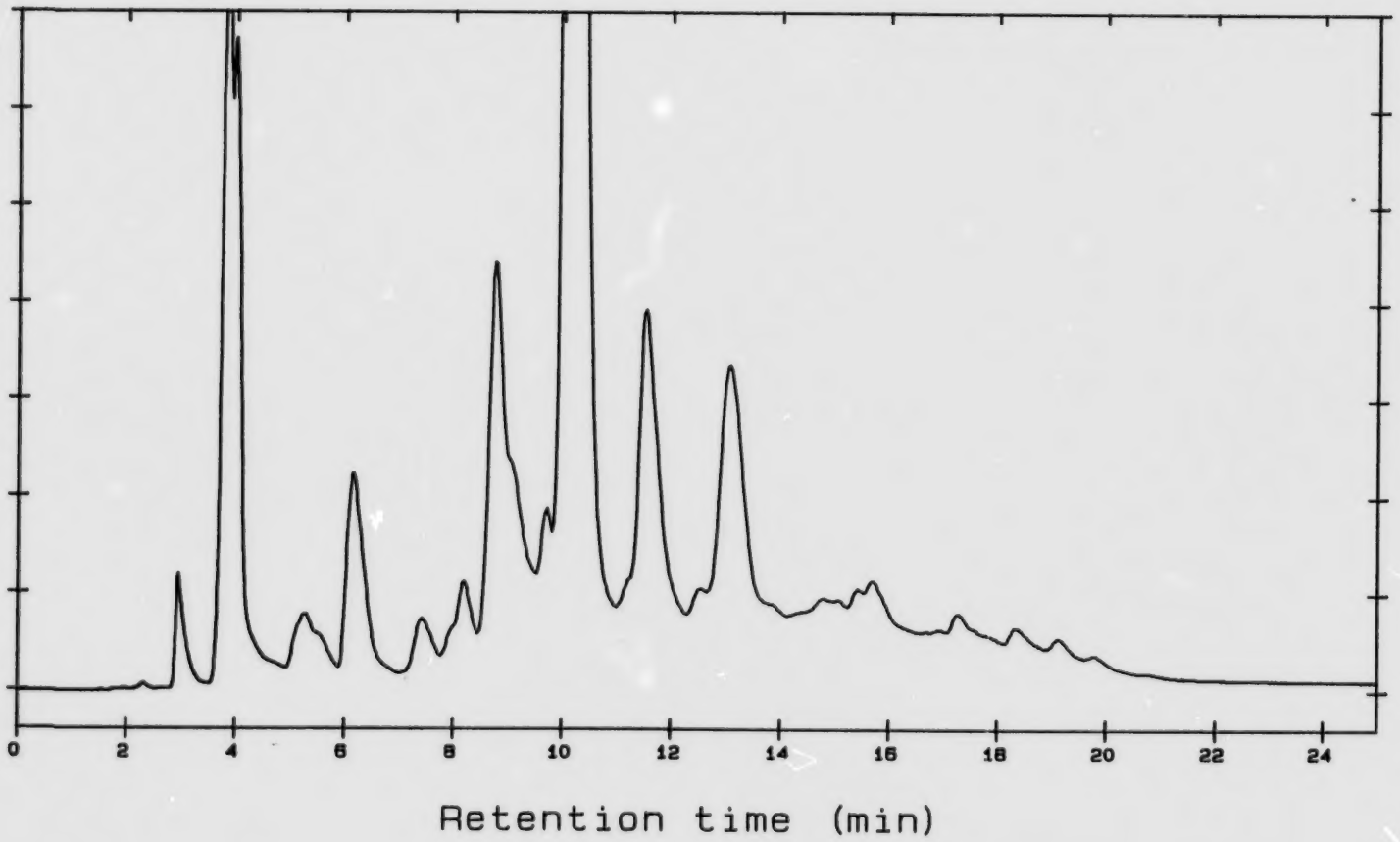


Figure 9: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Partisil ODS-3, 25 cm X 4.6 mm i.d..

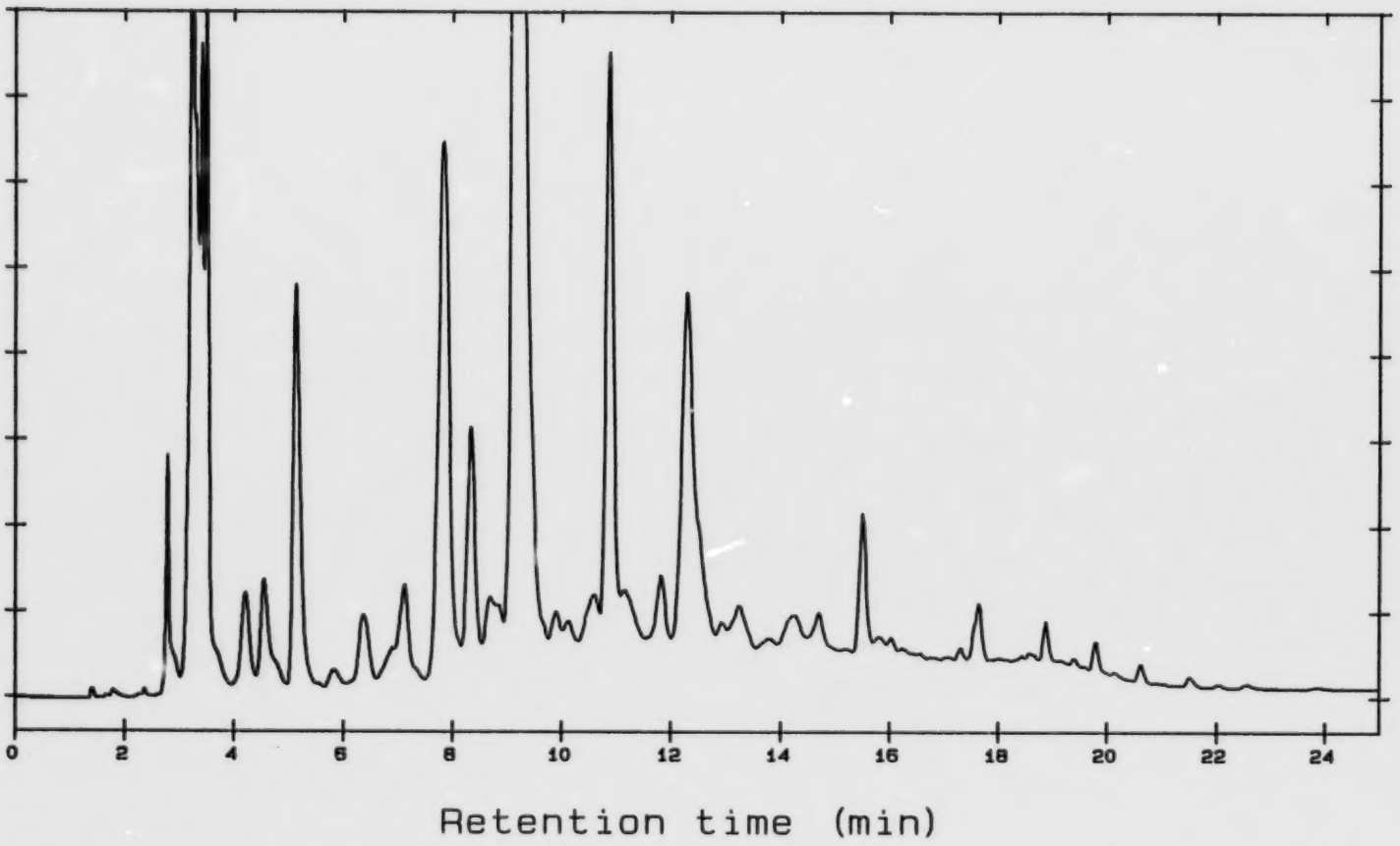


Figure 10: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Hypersil ODS, 25 cm X 4.6 mm i.d..

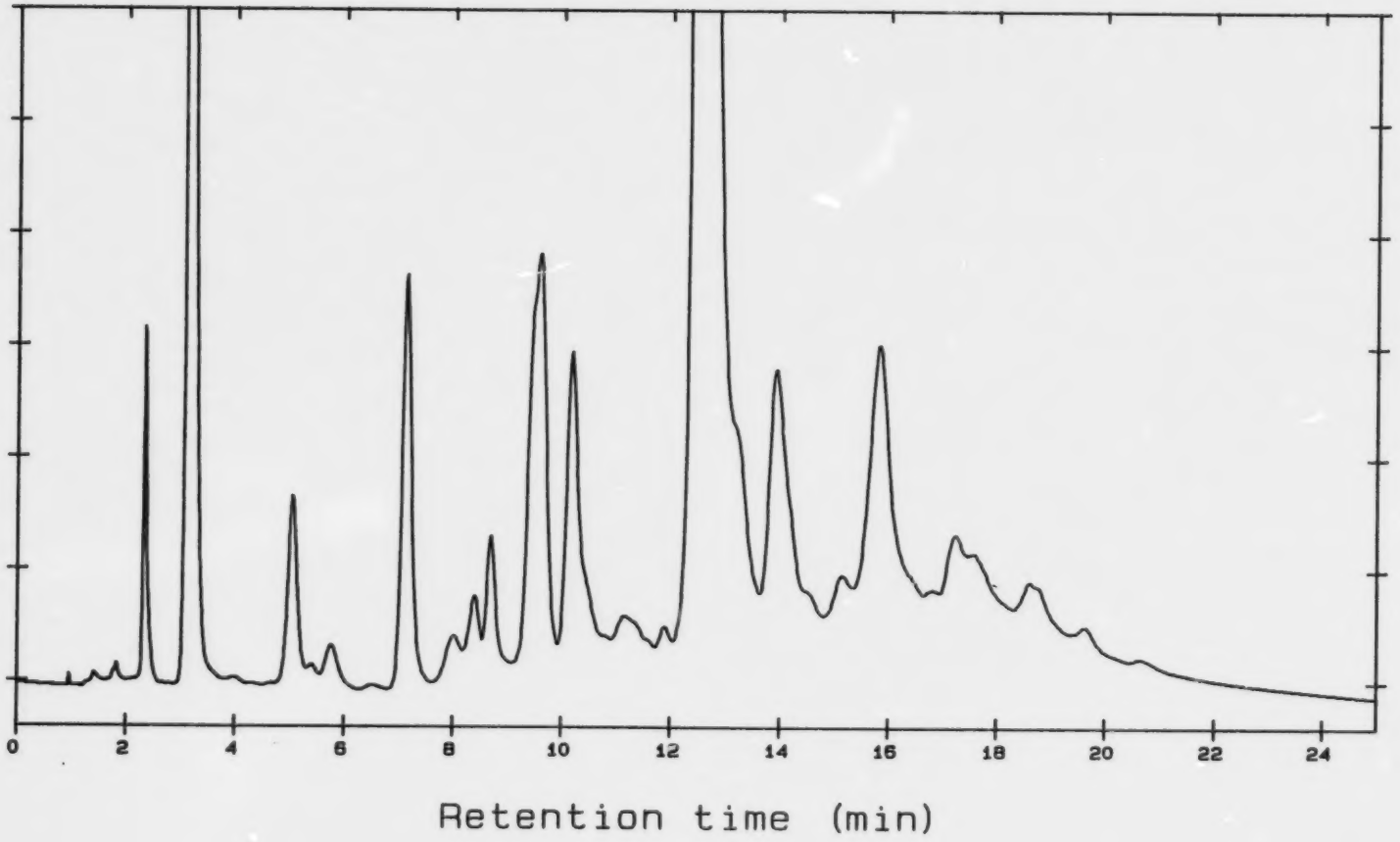


Figure 11: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: PRP-1, 25 cm X 4.1 mm i.d..

Columns #3 and #9 have a polymeric layer; the others have packings with monomeric layers.

Even with the best silanization conditions, it is not possible to bond alkyl chains to all the hydroxyl groups at the surface of the silica gel because there is steric hindrance. Of the 8 silanol groups per nm^2, a maximum of 4-5 can be bonded through the silanization procedure. There are always some silanol groups remaining on the surface of the particles and these can influence the selectivity of the stationary phase. To reduce this influence, silanol groups are "capped" with a second silanization reaction, usually involving a short organochlorosilane. Columns #1, #2, #5, #6, #7 and #8 are capped.

A comparison of the MCH-5-n-CAP (Figure 2) and MCH-10-n-CAP (Figure 4) columns shows slightly improved resolution with 5 µm particles. According to chromato - graphic theory, a decrease of the particle size increases the number of theoretical plates and thus the separation efficiency of a column. However, a shorter column packed with 5 µm particles (MCH-5-n-CAP, 15 cm long) has significantly lower efficiency, as shown in Figure 5. It is clear from these figures that good separation of an epoxy resin system cannot be achieved on too short a column packed with 5 µm particles. A minimum length of 25 cm is necessary.

A comparison of Figures 4 and 6 shows the influence of the capping on the column efficiency. The MCH-10-n-CAP column (Figure 4) gives somewhat better resolution than the MCH-10 column (Figure 6), which is not capped. The best columns, Hypersil MOS-1 and MCH-5-n-CAP, are both capped with trimethylsilyl groups.

For the separation of epoxy resin systems, polymeric coverage gives unacceptable results as shown for the CH-10 column (Figure 7) and the Partisil ODS-2 column (Figure 8). This is especially true for the CH-10 column which is quite unsuitable for the analysis of Narmco 5208.

The Partisil ODS-3 column (Figure 9) shows that even if a monomeric layer and secondary capping are employed, inefficient separation can result. With this column, the percentage of bonded silanol groups on the surface after the bonding reaction is extremely high, over 95%, compared to 75% for the Partisil ODS-2 (Figure 8). Thus, the "degree of non-polarity" is too high with the Partisil ODS–3 packing to efficiently separate more polar compounds such as those found in an epoxy resin system.

This is confirmed with the separation obtained with the Hypersil ODS column (Figure 10). The separation is not bad but it is not as good as for the Hypersil MOS-1 (Figure 3), which is more polar than Hypersil ODS. In addition, the peak of the hardener at 3.2 minutes shows structure which is not observed in Figure 3.

A special case is illustrated with the PRP-1 column in Figure 11. This stationary phase is a rigid macroreticular styrene-divinylbenzene copolymer of spherical shape. Its main advantage is that it can resist a strongly acidic (pH = 1) or basic (pH = 13) environment. Bonded silica, on the other hand, has a useful pH range between 2.0 and 8.5. This is extremely useful for ionizable compounds but for epoxy resin systems, the resolution is inadequate.

In conclusion, the reverse-phase packing should be slightly polar (C8 chains), monomeric, and capped to obtain a good separation of epoxy resin systems. However, if only a few peaks are of interest for quality control, the separation does not require an excellent resolution.

3.3.4 Detection

An epoxy resin system contains many compounds with different structures and properties. Ideally, a universal detector such as a refractive index detector should be used. However, gradient elution is impossible with this detector because the refractive index of the eluent is continuously changing during the experiment and a variation of the baseline is observed as the composition of the mobile phase is modified.

The UV detector is more suitable for analysing epoxy resins. Figures 12 to 15 show chromatograms obtained on a Hypersil ODS column at four different wavelengths: 200 nm, 230 nm, 254 nm, and 280 nm. In order to properly compare the chromatograms, they are shown at the same attenuation.

At 200 nm (Figure 12), all the peaks are detected very well but the baseline is not stable. The variation of the eluent composition is detected at this wavelength and this is reflected in the baseline. Also, there is a greater possibility of error since impurities in solvents can easily be detected and can significantly affect the measurement of the peaks. Thus, reproducible quantitative results are more difficult to obtain under these conditions. At 230 nm (Figure 13), the same compounds are detected as at 200 nm, but the level of variation of the baseline is considerably decreased. At 254 nm (Figure 14), aromatic compounds absorb more strongly than at 230 nm, but some peaks are almost undetected. For example, all the peaks after 15 minutes are not detected at 254 and 280 nm. At 280 nm (Figure 15), this phenomenon is amplified and this wavelength is certainly the worst choice. Thus, a wavelength of 230 nm seems most appropriate for detecting all the compounds in the epoxy resin system and it was chosen for subsequent experiments.

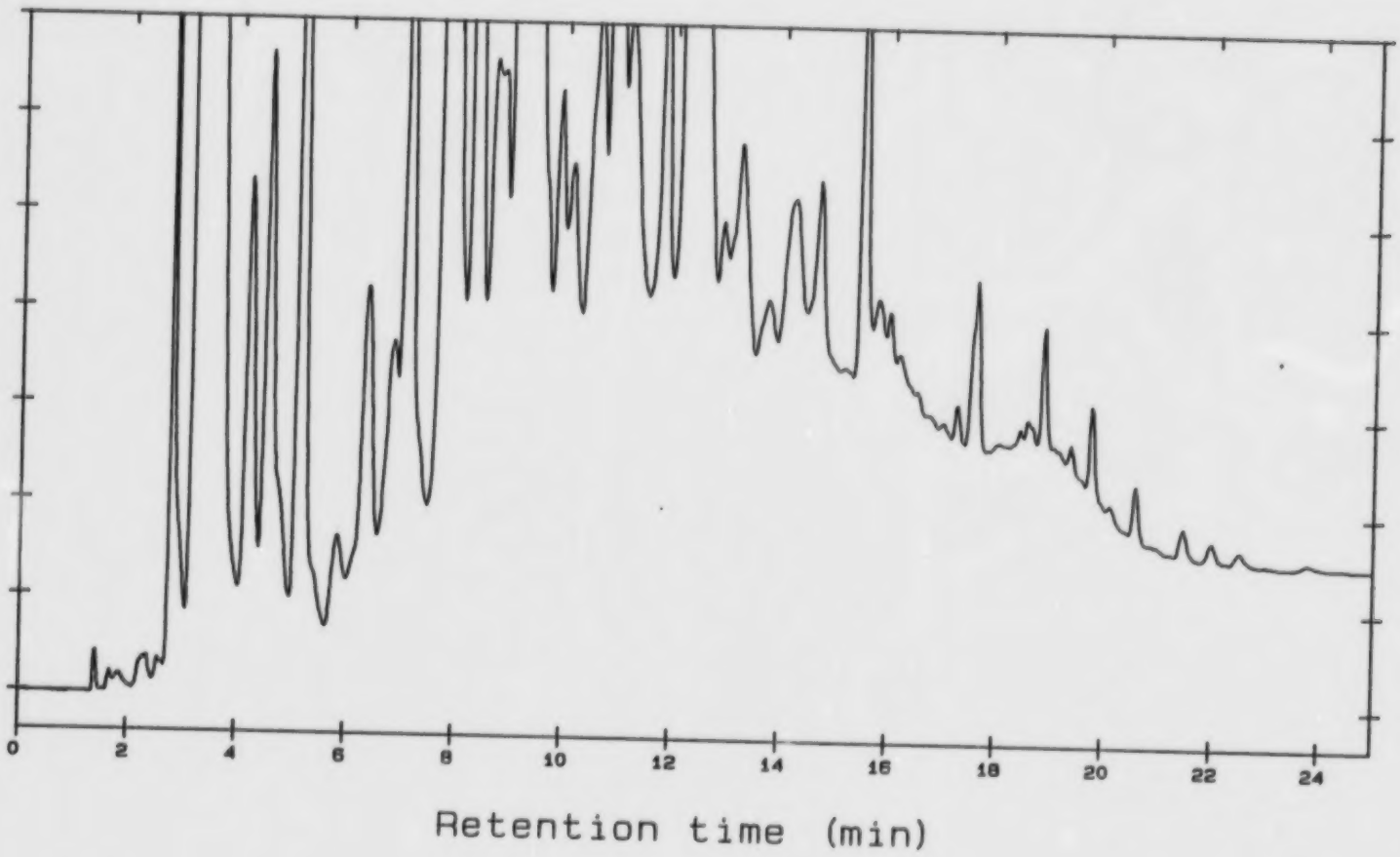


Figure 12: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Hypersil ODS, 25 cm X 4.6 mm i.d.; detection: 200 nm.

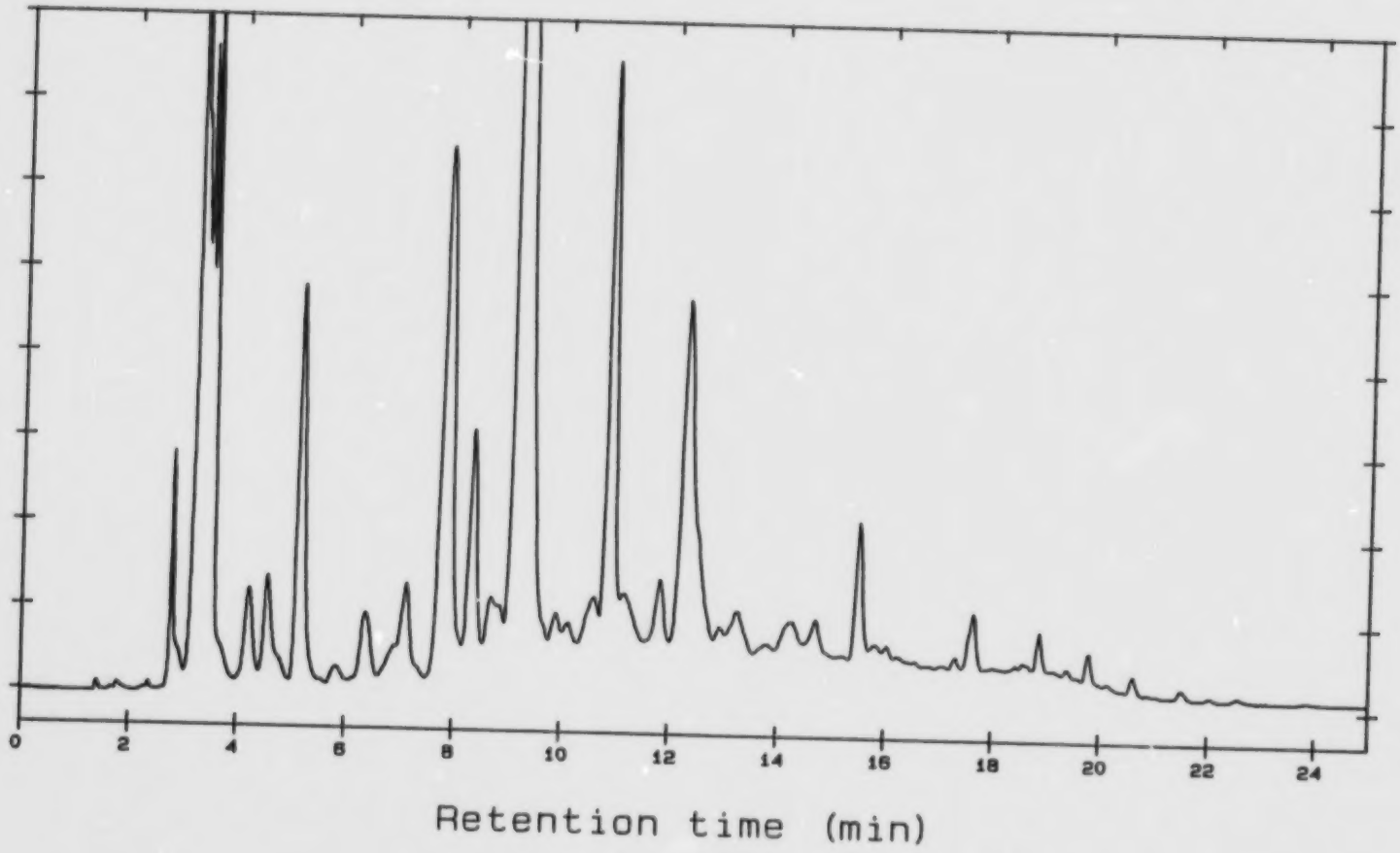


Figure 13: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Hypersil ODS, 25 cm X 4.6 mm i.d.; detection: 230 nm.

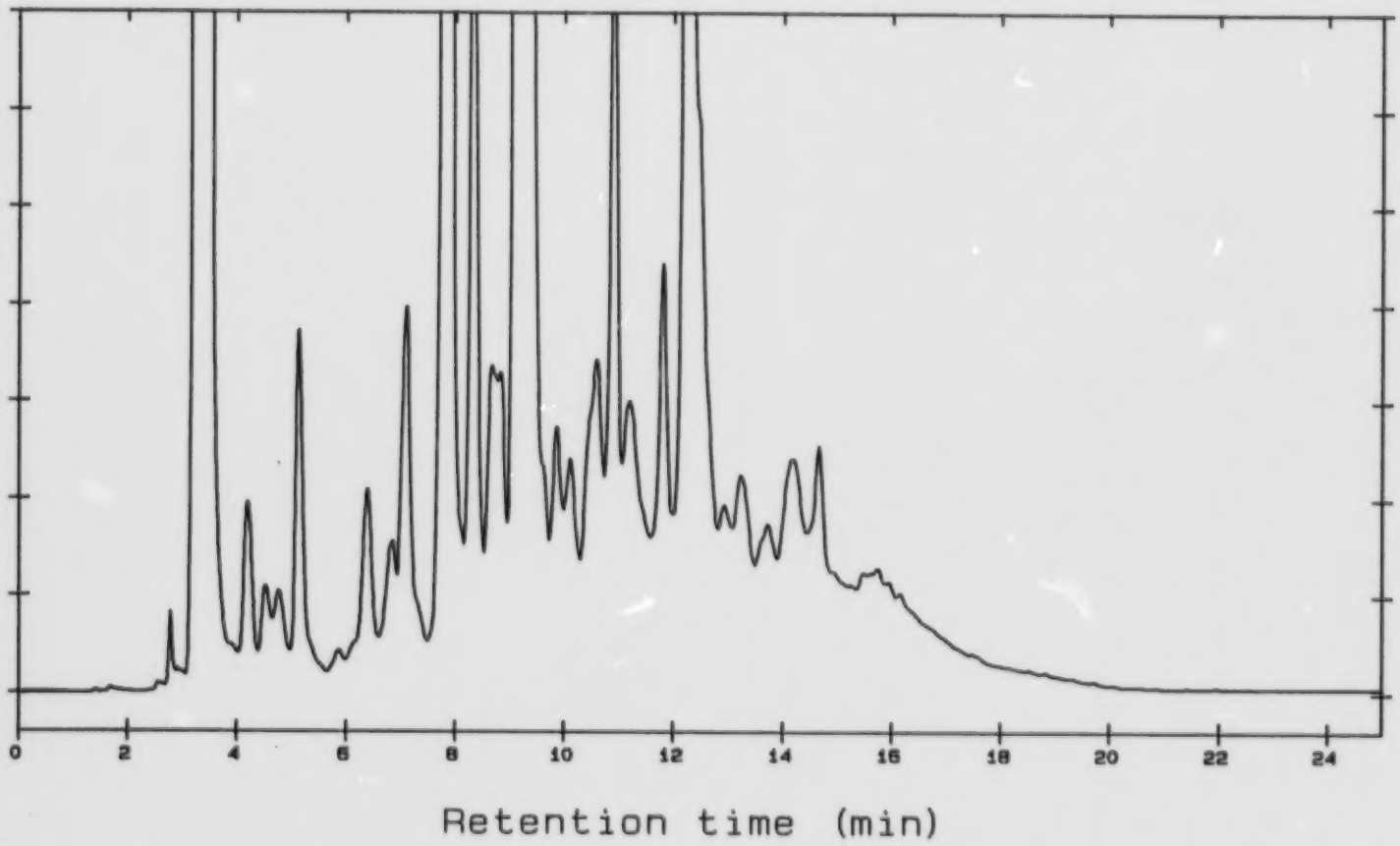


Figure 14: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Hypersil ODS, 25 cm X 4.6 mm i.d.; detection: 254 nm.

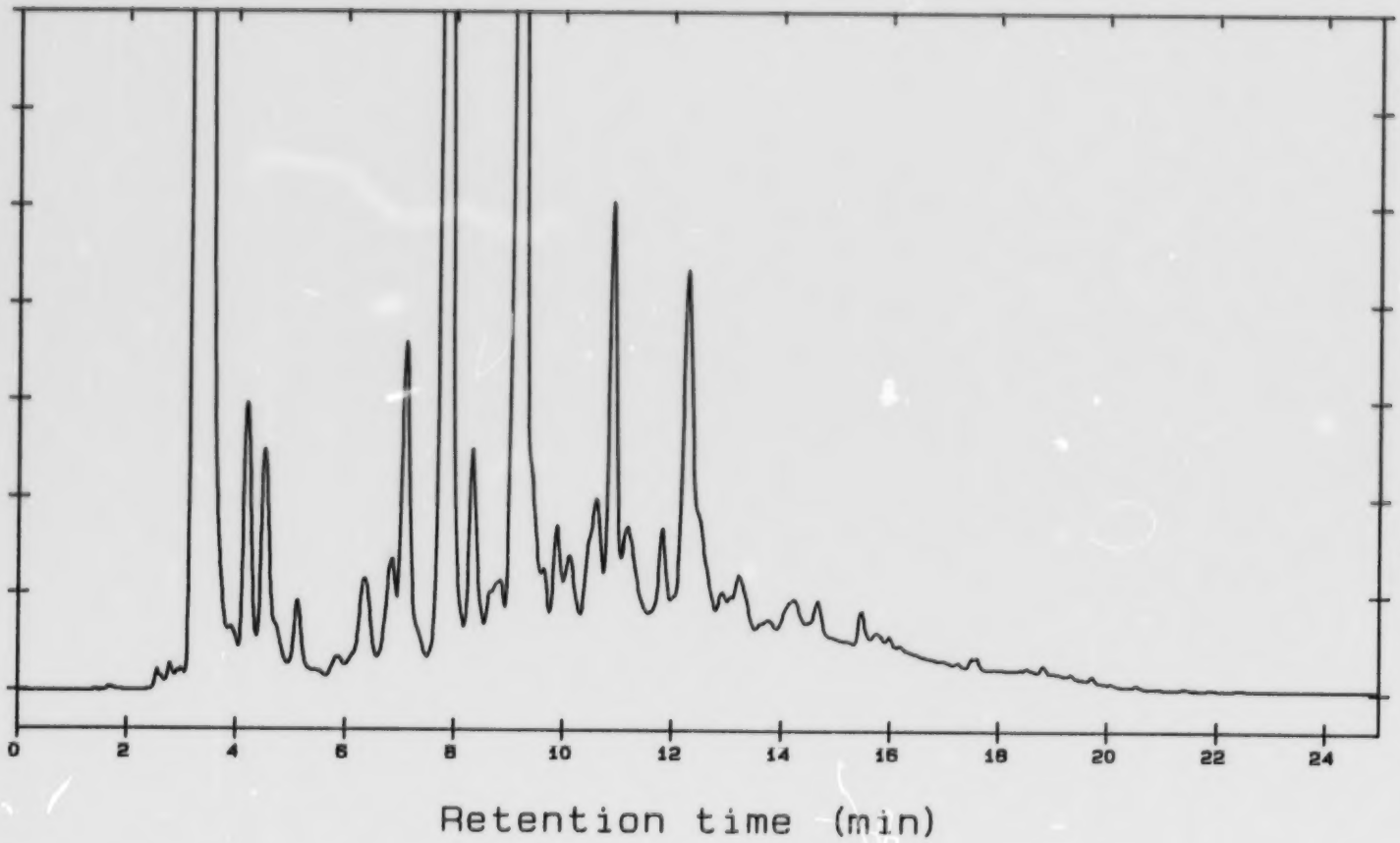


Figure 15: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: Hypersil ODS, 25 cm X 4.6 mm i.d.; detection: 280 nm.

3.4 Identification of LC peaks

3.4.1 Comparison with retention times of individual components

The chromatogram of the epoxy resin has many peaks as shown in Figure 2. It is very difficult to identify all the peaks but the main ones must be known in order to characterize the system. Figure 16 shows a chromatogram of Narmco 5208 neat resin, batch #1023; it is similar to that of the resin obtained from the prepreg (Figure 2). These chromatograms were obtained with the MCH-5-n-CAP column.

The first peak at 2.9 minutes and the peak at 6.1 minutes (peak #3) correspond to THF or impurities in THF. The peak at 3.9 minutes (#1) corresponds to the hardener DDS. Figure 17 shows the chromatogram of Ciba-Geigy Hardener HT 976 which consists mainly of DDS. The main peak at 3.9 minutes corresponds to the DDS, and the peak at 7.4 minutes is due to acetophenone which was added as internal standard. Other peaks at 5.6, 6.2, and 8.7 minutes are impurities in the HT 976 or THF.

Figure 18 shows the chromatogram of Araldite MY 720 epoxy resin, which is based on TGDDM. A TGDDM resin is the main component of the Narmco Rigidite 5208 system. The peak at 7.3 minutes is the acetophenone peak and the peak at 12.4 minutes corresponds to the monomer TGDDM. Other peaks are not identified but they are related to different modifications or oligomers of this product [7].

Figure 19 shows the chromatogram of Epi-Rez SU-8 epoxy resin, which is similar to the minor epoxy resin used in the Narmco 5208 system. The main compound, which is the monomer DGEBA (diglycidyl ether of bisphenol A), corresponds to the peak at 13.8 minutes. This product contains many oligomers as shown by the presence of many peaks at the end of the chromatogram.

3.4.2 Infrared spectroscopy of LC peaks

The compounds corresponding to the major peaks in the chromatogram of Narmco 5208 resin were collected manually in order to record their infrared spectra.

The first peak analysed by IR is peak #9 in Figure 16. According to the retention time, it should correspond to the main epoxy monomer TGDDM. The spectrum was taken using the ATR technique (described in Part 2) and it is given in Figure 20. Comparison

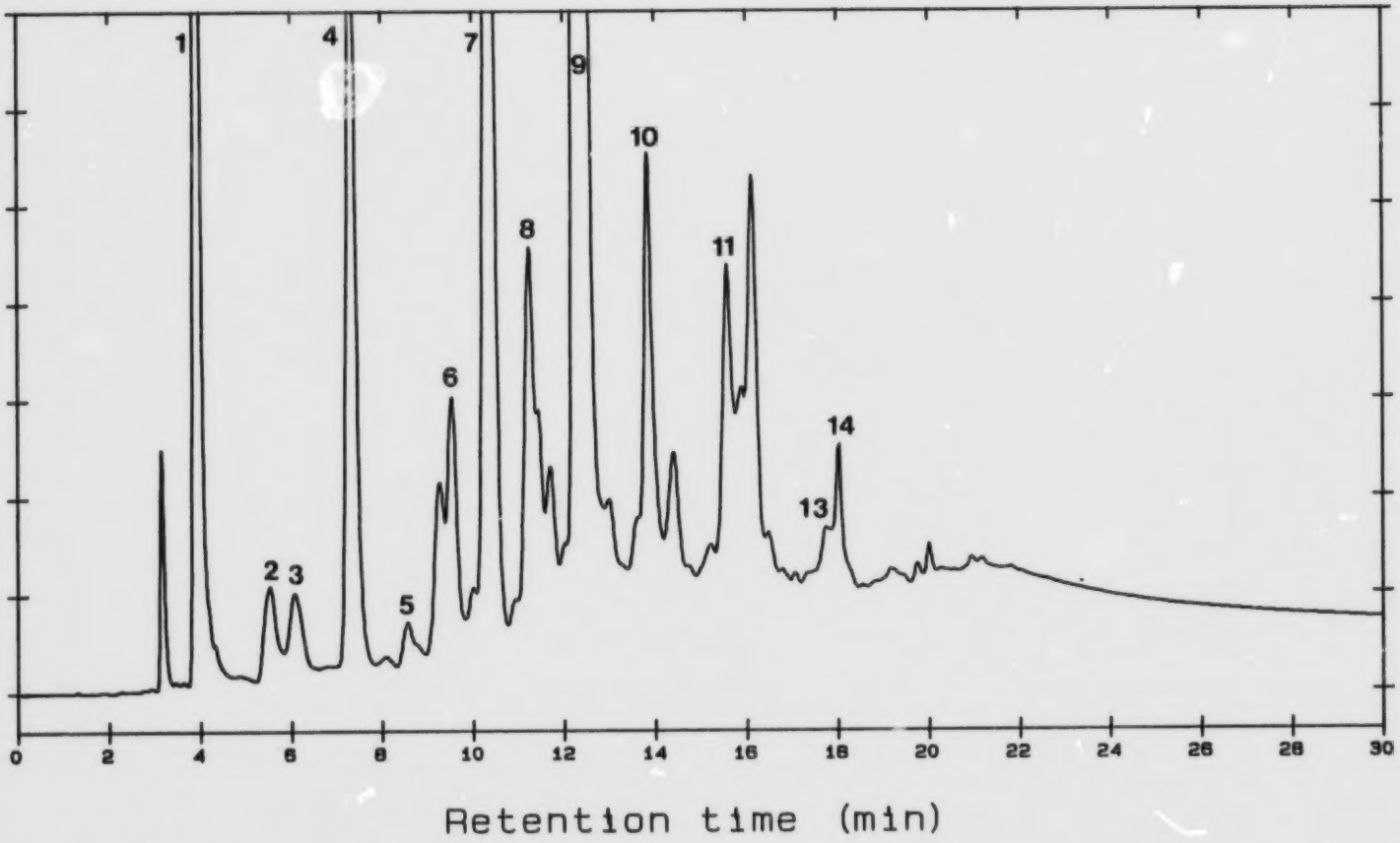


Figure 16: RPLC separation of Narmco 5208 neat resin, batch #1023, solution in THF. Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d..

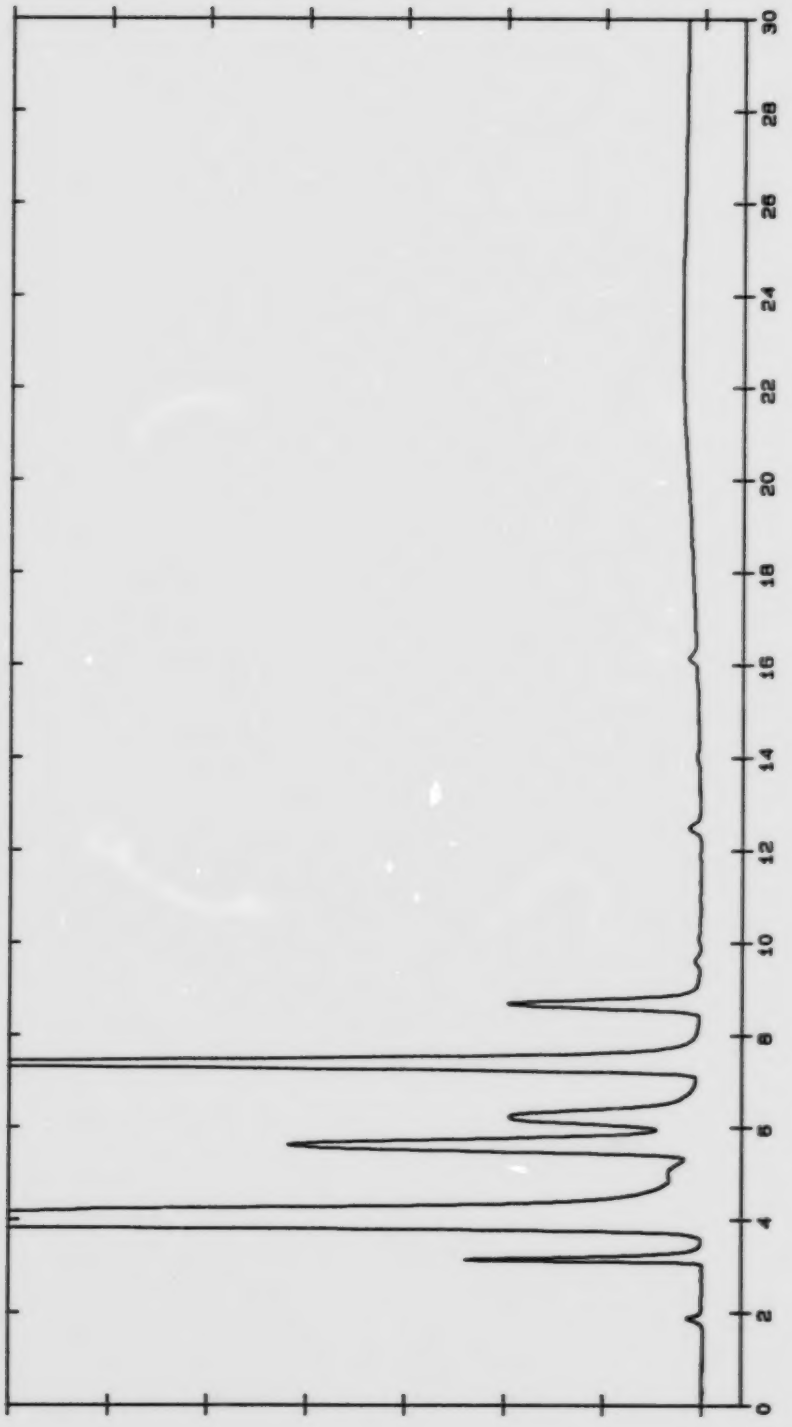


Figure 17: RPLC separation of Ciba-Geigy Hardener HT 976 in THF.
Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d..

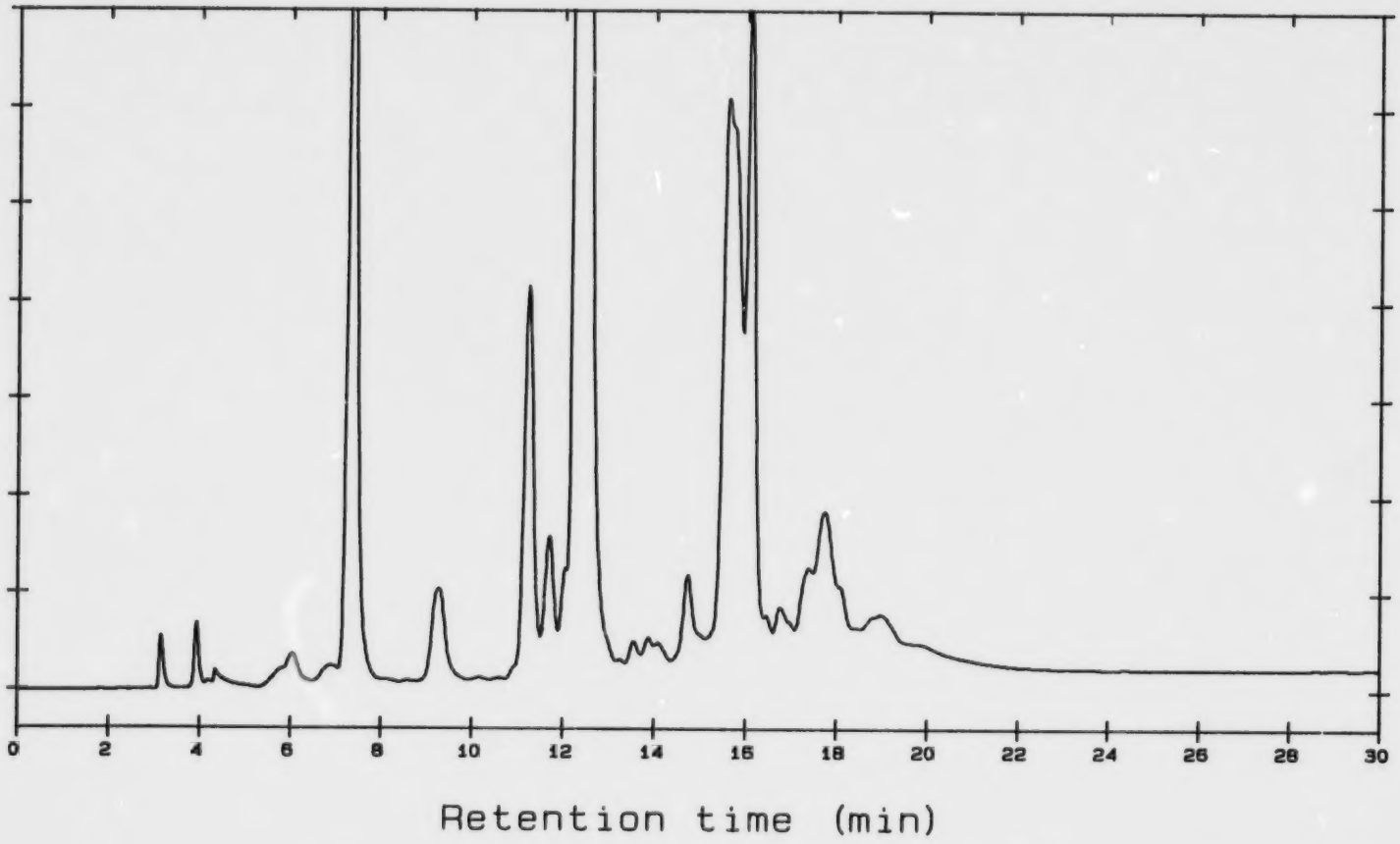


Figure 18: RPLC separation of Ciba-Geigy Araldite MY 720 in THF.
Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d..

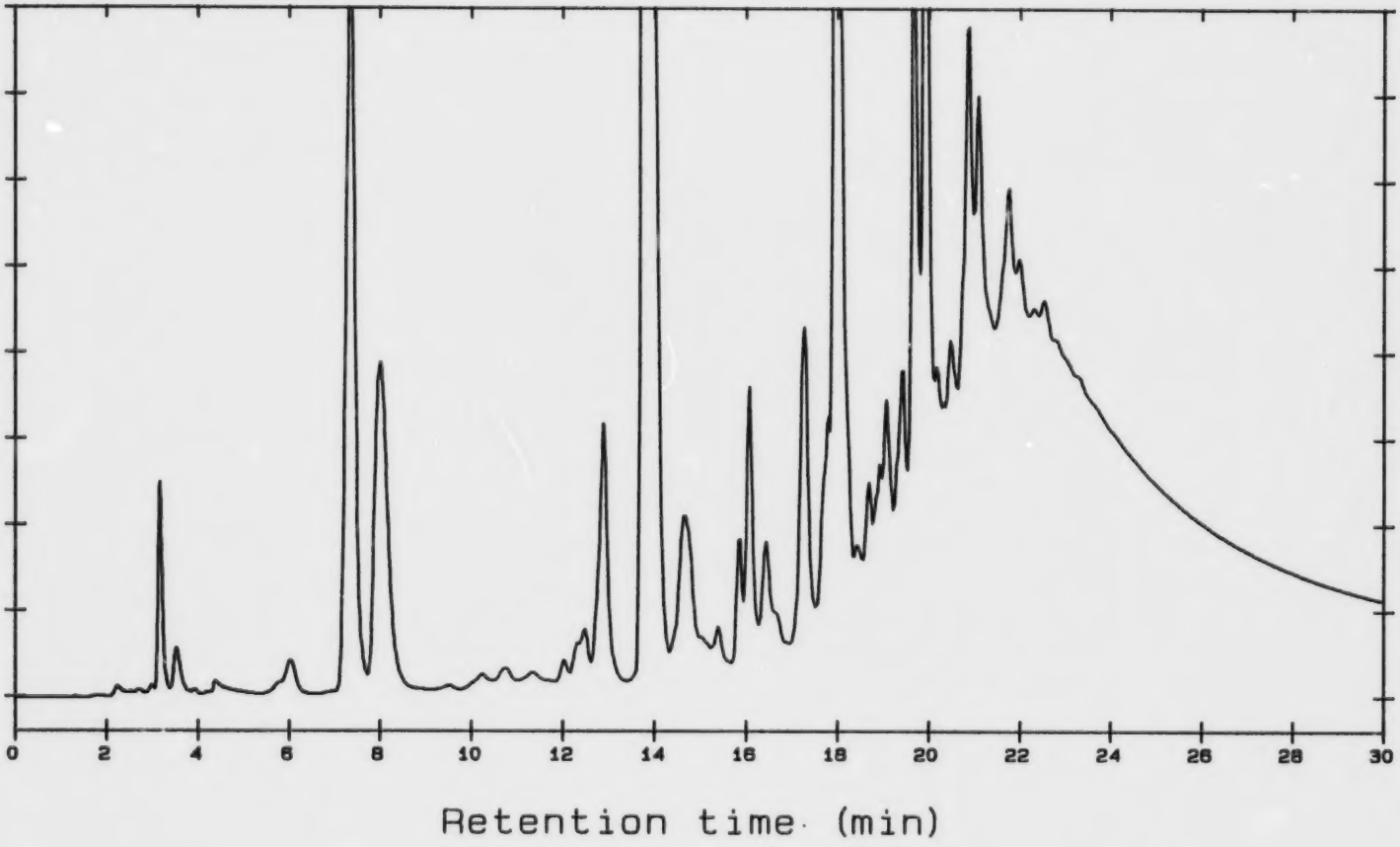


Figure 19: RPLC separation of Celanese Epi-Rez SU-8 in THF
Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d..

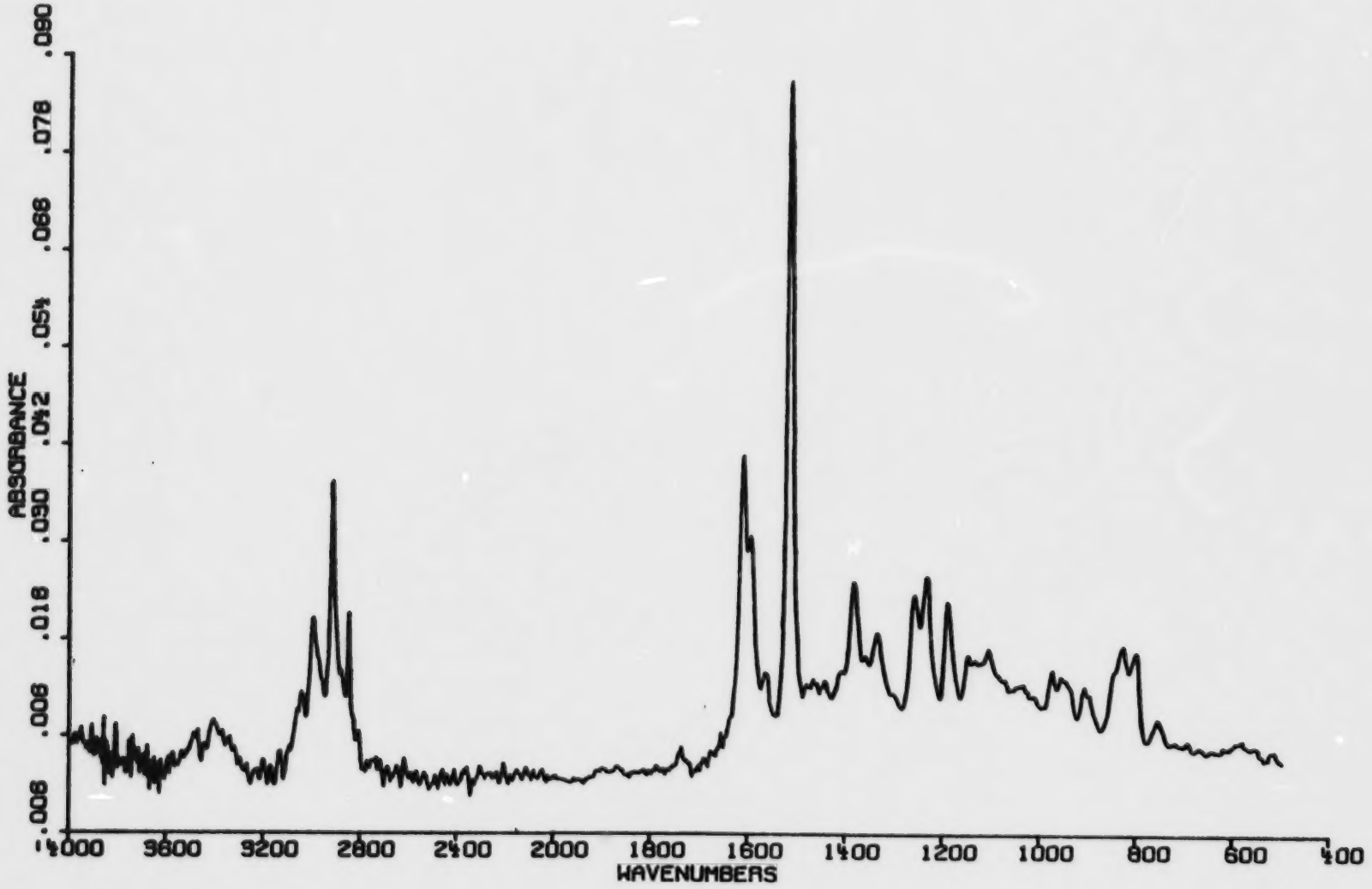


Figure 20: Infrared spectrum of peak #9 (Figure 2).

with Figure 5 of Part 2 confirms that peak #9 is TGDDM. The band assignment has been discussed in Part 2 and will not be repeated here. An NMR spectrum of the same fraction was also taken and provided further confirmation of the peak's identity.

According to the retention time, peak #1 corresponds to the hardener DDS. The IR spectrum is given in Figure 21 and, although it is not of the highest quality, it corresponds relatively well to the infrared spectrum of Hardener HT 976 (Figure 6 in Part 2). Thus, it is possible to confirm that peak #1 corresponds to the hardener DDS.

For the minor epoxy, which corresponds to peak #10 according to the chromatogram of Epi-Rez SU-8, it was impossible to obtain a good IR spectrum. However, on the basis of our results and those of Sewell [8], it is highly probable that this peak corresponds to the DGEBA monomer.

Finally, the infrared spectrum of peak #7 was recorded (Figure 22). It shows an amine N-H stretching band around 3400 cm^{-1}, a shoulder at 1626 cm^{-1} corresponding to N-H deformation, asymmetric and symmetric SO_2 bands at 1293 and 1146 cm^{-1} respectively, a C-S band at 1105 cm^{-1}, and epoxy bands around 900 cm^{-1}. As this spectrum contains bands characteristic of the hardener and of the main epoxy TGDDM, it is highly probable that this peak corresponds to the reaction product involving one molecule of TGDDM and one molecule of DDS. This hypothesis will be confirmed in Section 3.8.

Other peaks have not been identified because the amounts were too low to obtain good IR spectra and allow a formal identification.

3.4.3 Peak assignment on Hypersil MOS-1

It was shown in Section 3.3.3 that the Hypersil MOS-1 column is the most efficient for the separation of the Narmco 5208 resin. The chromatogram corresponding to this separation was compared with those of Hardener HT 976, Araldite MY 720, and Epi-Rez SU-8 so as to assign each peak to one of these products. The result is shown in Figure 23.

The two peaks marked with an asterisk were not observed in any of the three starting materials examined here. They could be due to an impurity in one of the particular batches used to make the prepreg or they could result from a coupling agent used to treat the surface of the graphite fibre reinforcement. They do not appear to be due to a reaction product since they do not become more intense when the prepreg is heated.

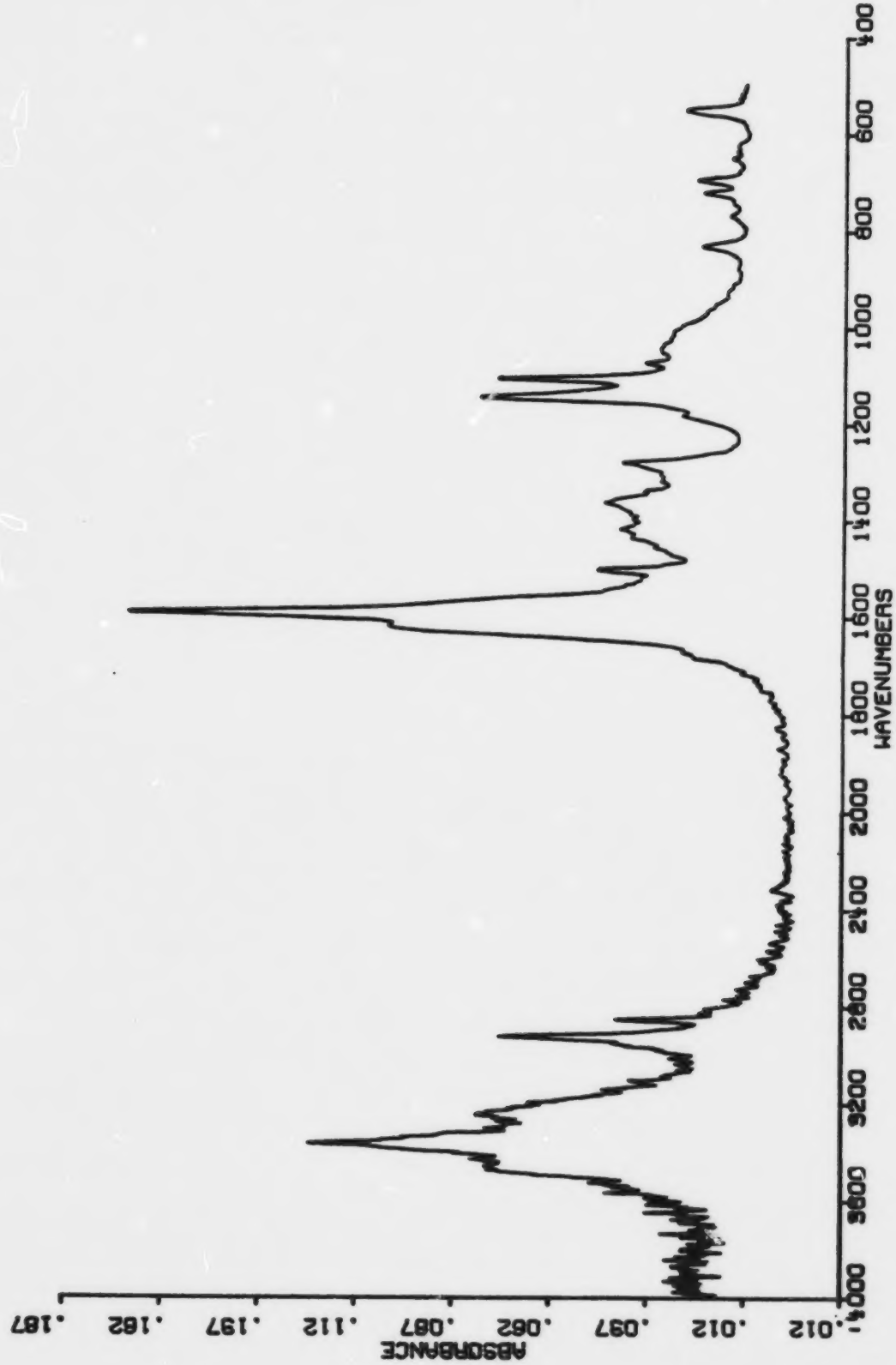


Figure 21: Infrared spectrum of peak #1 (Figure 2).

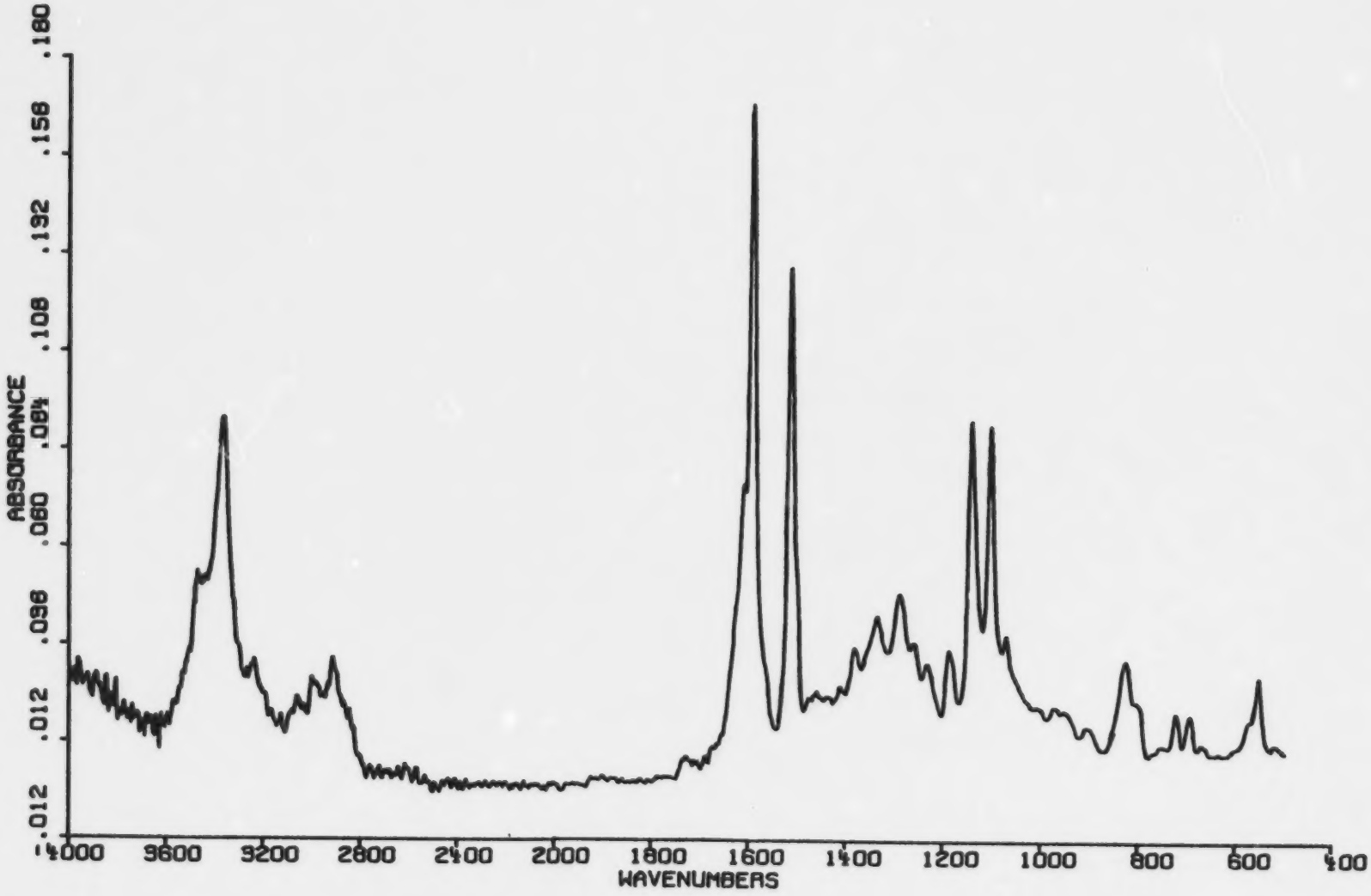


Figure 22: Infrared spectrum of peak #7 (Figure 2).

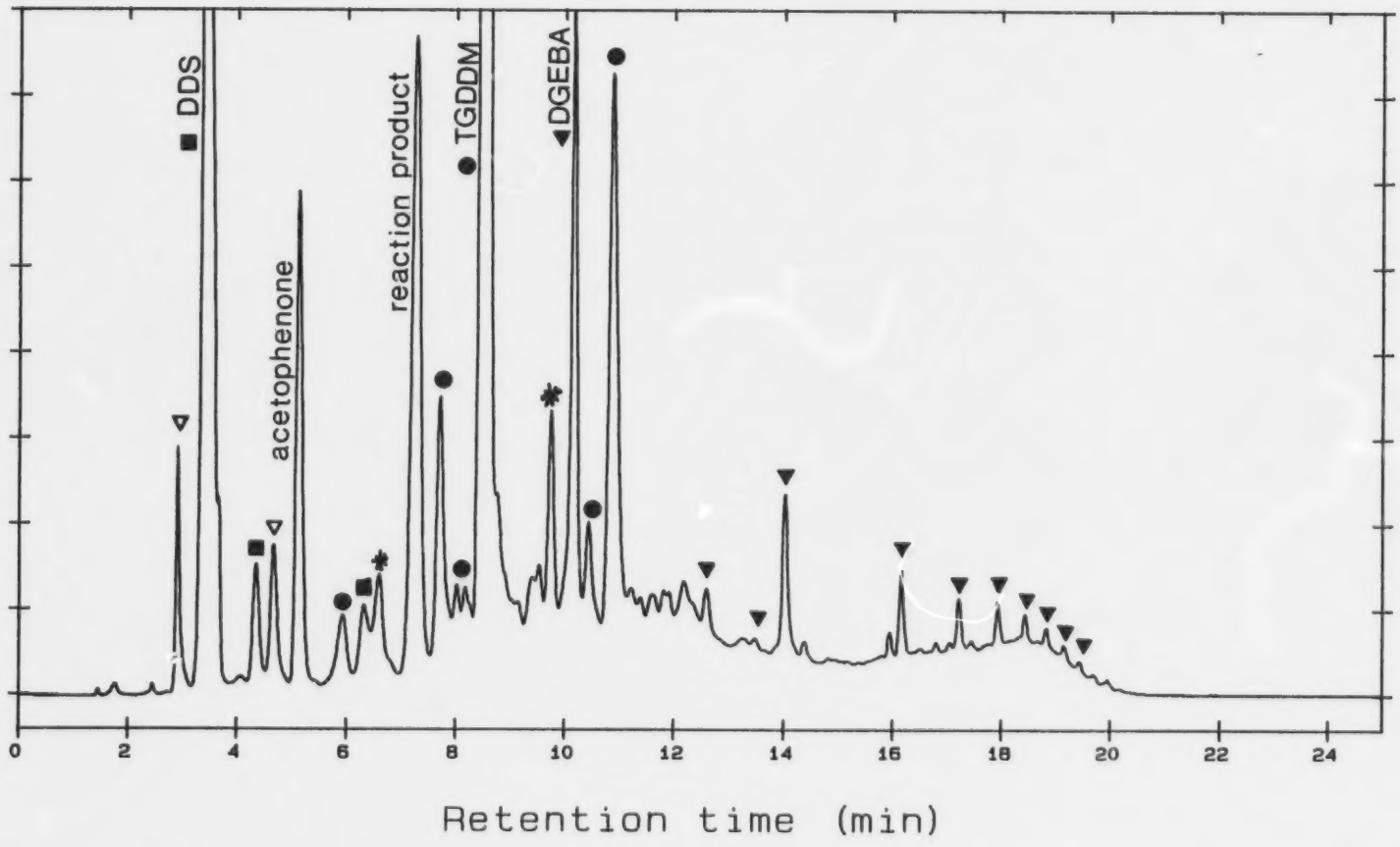


Figure 23: RPLC separation of the extract of Narmco 5208 prepreg, batch #1103, for components identification.
Column: Hypersil MOS-1, 25 cm X 4.6 mm i.d.
(▽) THF; (●) MY 720; (■) HT 976; (▼) SU-8.

3.5 Reproducibility of LC methods

3.5.1 Description of the methods of calculation

There are various methods for the quantitation of the peaks in the chromatogram. Four of them will be reviewed to point out their advantages and disadvantages. In the following discussion, no distinction will be made between peak area and peak height. The term area will be used but it should be read as either area or height.

The simplest method is the measurement of the peak area (raw data). However, this method is not reliable as there are several sources of variation which can influence the results, such as instrumental response, errors in concentration, weighing, solvent evaporation, and injection.

The second method involves taking the ratio of the peak area with respect to that of the TGDDM peak. This method eliminates many sources of error and it is also simple to use. However, it gives results which correspond to the ratios of compounds present and can therefore detect only variations in these ratios. Thus, an impurity which gives a peak separate from the peaks analysed could be present in a significant amount but would not affect the calculated ratios.

A third method is to determine the relative area of peaks with respect to the total area of the chromatogram. This method is similar to the previous one but it will be sensitive to any new peaks which may appear. However, there are problems with the establishment of a reproducible baseline for the integration of all peaks, and this method will not detect impurities which do not give peaks in the chromatogram.

The last method involves using an internal standard to quantitate the peaks. This is the most precise method because it gives a result which is directly related to the percentage by weight of the compound in question. It could detect even impurities which do not appear in the chromatogram, if they are present in significant amounts. However, this method is more complicated, requires more care, and can be subject to weighing errors during the preparation of solutions. These methods will be examined in detail in the following sections.

3.5.2 Internal standard

For quantitative work, it is advisable to include in the solution an internal standard which can be added in known amounts and used as a reference for the analyte peaks.

Certain general requirements have been reported for the choice of an internal standard [9,10]:

(i) The internal standard should be completely resolved in the chromatogram from the other known and unknown substances;
(ii) It should be eluted near the peak of interest;
(iii) The peak height (or peak area) of the internal standard should be similar to that of the substance to be determined;
(iv) It should be chemically similar to the substance of interest;
(v) It should be chemically stable and commercially available in high purity.

Obviously, it is not always easy to find a compound which meets all these requirements. For the analysis of the epoxy resin system, different compounds were tested with the ACN/H_2O gradient described in Section 3.3.2. As there is a "vacant" region available between 7.0 and 8.5 minutes (Figure 2), the internal standard should elute in this region. Table 4 gives the retention times of some compounds with this gradient elution method.

Table 4. Retention times of some compounds on an MCH-5-n-CAP column, 30 cm long x 4 mm i.d., with chromatographic conditions as described in Section 3.3.2.

Compound	Retention time (min)
p-xylene	13.6
toluene	11.8
benzene	9.6
benzaldehyde	7.2
acetophenone	7.5

The first three solutes are inappropriate as regards the retention time; they are eluted in the same region as other peaks. Benzaldehyde has a suitable retention time but it seems difficult to obtain commercially with sufficient purity, since injection of this product gave several peaks in the chromatogram. The best internal standard was acetophenone.

In the analysis of Narmco 5208, acetophenone was added at a concentration of about 100 µg/mL to a solution containing approximately 600 mg of resin in 100 mL of THF. To account for variations in the weight of resin, after the peak areas or peak heights are ratioed against that of acetophenone they are normalized to a standard resin weight of 100 times the acetophenone weight. This gives normalized peak intensities in the range of 0.2 to 20. Thus:

$$\text{Normalized response} = \frac{\text{Response of peak}}{\text{Response of acetophenone}} \times \frac{\text{Wt. acetophenone (g)}}{\text{Wt. of resin (g)}} \times 100$$

For each peak, this normalized response is directly related to the percentage by weight of the compound in question in the resin system. This method eliminates to a large extent the effects of variations in instrumental response and loss of solvent from the solution.

3.5.3 Direct addition of acetophenone to the prepreg extract - manual injection of the sample

A normalization procedure has been described in the preceding section. In a first experiment, a known quantity of acetophenone (10 µL, 10.28 mg) was directly added with a microsyringe to the prepreg extract. The total volume of the solution was around 100 mL and it generally contained about 600 mg of resin. The reproducibility with respect to the extraction was checked by analysing three different extractions of resin from the Narmco 5208 prepreg, batch #1103. The percentages by weight of resin extractedwere respectively 40.15%, 39.23%, and 38.82%. The reproducibility with respect to manual injection on the chromatographic column was checked by performing four injections of one of the prepreg extracts.

3.5.3.1 Results based on peak area

The four methods described in Section 3.5.1 were used to evaluate quantitatively the detector response based on peak areas. The following four tables show average results and standard deviations calculated using: (i) absolute peak areas (Table 5); (ii) peak area ratios with respect to the TGDDM peak (Table 6); (iii) relative peak areas with respect to the total chromatogram (Table 7); (iv) normalized peak areas calculated using acetophenone internal standard (Table 8). The peaks of greatest interest are: #1 (DDS), #4 (acetophenone), #7 (reaction product), #9 (TGDDM), #10 (DGEBA). Peak #3 was not included in the calculations because it was found to be due to an additive or impurity in the THF.

Regardless of the method of calculation, the baseline used for the evaluation of the peak area or the peak height must be clearly established to avoid quantitation differences between the chromatograms. This requirement is extremely important for comparing results obtained over a long time interval or even for comparing results obtained on different columns. Thus, it is important to always draw the baseline at the same position on the chromatograms. Figure 24 gives an example of baselines selected for this set of extractions and injections. The ideal case consists of well resolved peaks where baselines are drawn from valley to valley. In a complex chromatogram such as that of an epoxy resin system, it is not always possible to apply this principle unequivocally. For the acetophenone peak (#4), there is no problem and the baseline is easy to draw. However, for peaks #8 and #9, the situation is more complicated. If the baseline is drawn from valley to valley as shown in Figure 24 by dotted lines, the peak area or height will be sensitive to the degree of resolution of the two peaks. An increase in resolution will increase the apparent peak areas, whereas a decrease will have the opposite effect. Thus, it is preferable to draw the baseline from the beginning of peak #8 to the end of peak #9. Generally, it is advisable to draw a baseline following the base level of the chromatogram to minimize the extent of variation in the measurement of peak area or peak height.

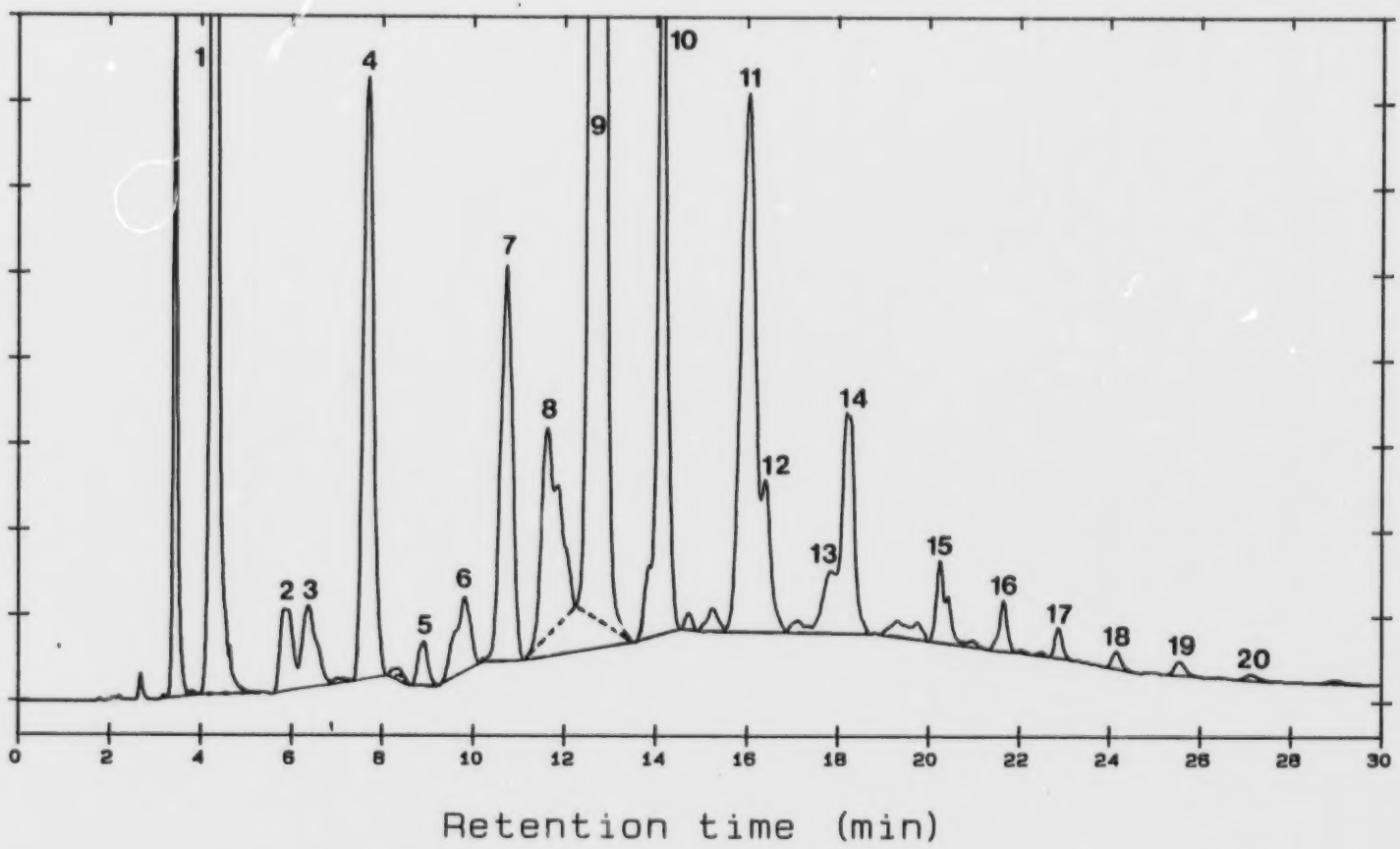


Figure 24: Drawing of the baseline on a chromatogram for quantitative measurements.
Column: MCH-5-n-CAP, 30 cm X 4.0 mm i.d.

Table 5 clearly shows that absolute peak area is not a good measure to evaluate the resin composition in the prepreg. As the amount of resin varies somewhat for each extraction, the relative standard deviation σ is high and the peak area or the peak height cannot be used.

Table 5. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using absolute peak areas; direct addition of acetophenone and manual injection.

Peak #	Average of three extractions			Average of four injections		
	Area	σ	σ (%)	Area	σ	σ (%)
1	28723	1294	4.5	29194	667	2.3
2	1438	203	14.1	1557	119	7.6
4	9915	228	2.3	9823	256	2.6
5	617	54	8.7	628	12	1.9
6	1684	103	6.1	1818	135	7.4
7	7193	462	6.4	7081	63	0.9
8	7688	375	4.9	7067	1744	24.7
9	81032	4750	5.9	81977	1424	1.7
10	11222	607	5.4	11396	241	2.1
11	11915	761	6.4	11832	71	0.6
12	2282	100	4.4	2578	314	12.2
13	1411	87	6.1	1318	52	4.0
14	4336	355	8.2	4382	158	3.6
15	1257	198	15.8	1270	127	10.0
16	667	27	4.0	668	50	7.4
17	357	18	5.0	360	8	2.2
18	224	14	6.1	230	10	4.3
19	246	14	5.6	243	4	1.6
20	117	11	9.1	119	10	8.4

Chen and Hunter [4] have proposed the use of the main epoxy peak, TGDDM, as a reference. The ratio DDS/TGDDM can be used to evaluate the resin composition and the ratio of the reaction product peak against the TGDDM peak serves to follow the aging of the resin. Table 6 shows the results obtained by dividing the peak areas by the area of the TGDDM peak (#9 in Figure 24) to give peak area ratios. The relative standard deviations are generally substantially lower than in the previous case. For the main peaks of interest (#1, #7, #10) they are of the order of 1% or less for the average of four injections, and

2.5% or less for the average of three extractions. This method may be adequate for quality control of a well-characterized prepreg system, but since it uses only the ratios of a few well-defined peaks, it may not be sensitive to all variations in composition which may occur.

Table 6. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using peak area ratios with respect to the TGDDM peak (#9); direct addition of acetophenone and manual injection.

Peak #	Average of three extractions			Average of four injections		
	Area	σ	σ (%)	Area	σ	σ (%)
1	0.3548	0.0061	1.7	0.3561	0.0023	0.6
2	0.0177	0.0019	10.6	0.0190	0.0016	8.4
5	0.00760	0.00029	3.8	0.00766	0.00020	2.6
6	0.02079	0.00057	2.7	0.0222	0.0016	7.1
7	0.0888	0.0022	2.5	0.0864	0.0010	1.1
8	0.0949	0.0013	1.4	0.086	0.023	27.2
10	0.1385	0.0010	0.7	0.13901	0.00091	0.6
11	0.1470	0.0023	1.6	0.1444	0.0031	2.1
12	0.02819	0.00079	2.8	0.0314	0.0038	12.2
13	0.01741	0.00019	1.1	0.01608	0.00095	5.9
14	0.0535	0.0020	3.8	0.0535	0.0031	5.7
15	0.0154	0.0019	12.5	0.0155	0.0021	13.4
16	0.00826	0.00082	9.9	0.00814	0.00059	7.2
17	0.00440	0.00008	1.7	0.00439	0.00018	4.1
18	0.00277	0.00011	3.9	0.00280	0.00011	3.9
19	0.00304	0.00013	4.1	0.00296	0.00007	2.4
20	0.00145	0.00006	4.0	0.00145	0.00011	7.9

Table 7 shows the results calculated using relative peak areas, defined as the peak area divided by the total area of the chromatogram; this procedure is sometimes called internal normalization. The relative standard deviations are similar to those of Table 6 (peak ratio method). However, when applied to different batches over a longer time interval, this method is subject to complications. The problem is that the results are affected by all the peaks in the chromatogram, and these can have different response factors. Consequently, the magnitude of the changes in the chromatogram may not be truly indicative of the importance of the compositional variations. For example, a highly-

absorbing material will have a large effect even if the quantities involved are only small, whereas a poorly-absorbing molecule will have little effect even if the variations involved are significant. Also, changes in the chromatogram may affect the drawing of the baseline and hence the calculation of the total area.

Table 7. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using relative peak areas with respect to total area of chromatogram; direct addition of acetophenone and manual injection.

Peak #	Average of three extractions			Average of four injections		
	Area	σ	σ (%)	Area	σ	σ (%)
1	15.86	0.25	1.6	15.93	0.12	0.8
2	0.790	0.084	10.7	0.849	0.067	7.9
5	0.340	0.013	3.9	0.3425	0.0081	2.4
6	0.929	0.019	2.1	0.991	0.066	6.7
7	3.968	0.078	2.0	3.864	0.047	1.2
8	4.244	0.034	0.8	4.36	0.10	2.4
9	44.71	0.36	0.8	44.73	0.23	0.5
10	6.194	0.015	0.2	6.217	0.016	0.3
11	6.573	0.083	1.3	6.46	0.15	2.3
12	1.261	0.038	3.0	1.40	0.17	11.9
13	0.7785	0.0063	0.8	0.720	0.046	6.3
14	2.390	0.087	3.6	2.39	0.13	5.6
15	0.690	0.087	12.6	0.694	0.093	13.3
16	0.369	0.036	9.8	0.364	0.027	7.4
17	0.1969	0.0019	1.0	0.1962	0.0078	4.0
18	0.1237	0.0040	3.2	0.1254	0.0043	3.4
19	0.1359	0.0046	3.4	0.1324	0.0029	2.2
20	0.0647	0.0029	4.4	0.0649	0.0051	7.8

The use of an internal standard such as acetophenone overcomes many of the disadvantages associated with the other methods. The results obtained using this method are given in Table 8. The relative standard deviation is slightly higher than for the previous two methods, but is under 4% for the main peaks. Although somewhat more complicated than the other methods, this one gives more information since the figures obtained are directly related to the percentage by weight of the compound in question in the resin system. Thus, even in the hypothetical case where the resin is contaminated by a foreign

material not detected by LC, the results will be affected if the amount is significant because the percentage by weight of all the measured components will be reduced. The use of peak ratios would not detect such contamination. The principal sources of error in the internal standard method occur in the weights of acetophenone (because of the small quantity involved) and of extracted resin (because of the possible presence of minute pieces of graphite fibre in the extracted resin solution).

Table 8. RPLC results for Narmco prepreg, batch #1103, calculated using normalized peak areas with respect to acetophenone internal standard; direct addition of acetophenone and manual injection.

Peak #	Average of three extractions			Average of four injections		
	Area	σ	σ (%)	Area	σ	σ (%)
1	4.810	0.079	1.6	4.888	0.028	0.6
2	0.240	0.032	13.1	0.261	0.023	8.8
5	0.1032	0.0067	6.5	0.1051	0.0037	3.6
6	0.282	0.010	3.6	0.304	0.021	6.8
7	1.204	0.046	3.8	1.186	0.026	2.2
8	1.288	0.023	1.8	1.18	0.31	26.5
9	13.56	0.42	3.1	13.73	0.15	1.1
10	1.879	0.046	2.5	1.908	0.022	1.2
11	1.994	0.073	3.6	1.982	0.063	3.2
12	0.382	0.010	2.6	0.431	0.049	11.4
13	0.2362	0.0079	3.3	0.221	0.014	6.4
14	0.725	0.043	5.9	0.734	0.050	6.9
15	0.210	0.032	15.1	0.213	0.031	14.7
16	0.1118	0.0086	7.7	0.1116	0.0070	6.3
17	0.0597	0.0012	1.9	0.0602	0.0031	5.1
18	0.0375	0.0015	4.0	0.0385	0.0016	4.1
19	0.0412	0.0015	3.6	0.0406	0.0014	3.4
20	0.0196	0.0014	7.0	0.0199	0.0014	7.0

Thus, the normalization procedure with an internal standard is preferable for evaluating the chromatogram of an epoxy resin system. Its main advantage is to eliminate the effects of variation in instrumental response and loss of solvent.

3.5.3.2 Results based on peak height

In isocratic elution, it has been shown that peak height measurements are more precise than peak area measurements [11]. Peak heights are less subject to interference by adjacent, overlapping peaks. For equivalent accuracy, less resolution is required for quantitation by peak height than by peak area.

Table 9 reports results obtained using normalization with acetophenone as internal standard but using the peak height instead of the peak area. A comparison with Table 8 shows that this gives lower relative standard deviations. The same trend is observed for the peak height divided by the peak height of TGDDM as shown in Table 10. The chromatogram of the epoxy resin system being complex, there are many overlapping peaks. Thus, accurate measurement of the area is more difficult.

Table 9. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using normalized peak heights with respect to acetophenone internal standard; direct addition of acetophenone and manual injection.

Peak #	Average of three extractions			Average of four injections		
	Height	σ	σ (%)	Height	σ	σ (%)
1	10.78	0.14	1.3	10.85	0.30	2.8
2	0.208	0.011	5.2	0.225	0.015	6.9
5	0.1108	0.0065	5.8	0.1110	0.0047	4.2
6	0.2036	0.0050	2.4	0.2097	0.0075	3.6
7	1.075	0.013	1.2	1.079	0.011	1.0
8	0.611	0.010	1.6	0.631	0.013	2.0
9	13.840	0.067	0.5	14.00	0.12	0.9
10	2.088	0.043	2.1	2.143	0.025	1.2
11	1.498	0.010	0.7	1.484	0.018	1.2
12	0.442	0.022	4.9	0.528	0.098	18.5
13	0.1853	0.0057	3.1	0.1820	0.0091	5.0
14	0.6127	0.0017	0.3	0.612	0.011	1.8
15	0.2270	0.0018	0.8	0.2299	0.0064	2.8
16	0.1442	0.0077	5.3	0.1475	0.0074	5.1
17	0.0876	0.0041	4.6	0.0876	0.0025	5.6
18	0.0516	0.0027	5.3	0.0514	0.0039	5.5
19	0.03957	0.00036	0.9	0.03909	0.00031	0.8
20	0.01773	0.00092	5.2	0.0177	0.0012	6.9

Table 10. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using peak height ratios with respect to the TGDDM peak (#9); direct addition of acetophenone and manual injection.

Peak #	Average of three extractions			Average of four injections		
	Height	σ	σ (%)	Height	σ	σ (%)
1	0.7790	0.0062	0.8	0.775	0.024	3.1
2	0.01503	0.00078	5.2	0.0161	0.0011	6.6
4	0.1200	0.0027	2.2	0.1174	0.0010	0.9
5	0.00801	0.00046	5.7	0.00793	0.00030	3.8
6	0.01472	0.00040	2.7	0.01498	0.00055	3.7
7	0.0777	0.0013	1.7	0.07704	0.00056	0.7
8	0.04412	0.00055	1.2	0.04506	0.00091	2.0
10	0.1508	0.0030	2.0	0.1531	0.0019	1.2
11	0.10820	0.00019	0.2	0.1060	0.0016	1.5
12	0.0319	0.0015	4.7	0.0377	0.0070	18.6
13	0.01339	0.00035	2.7	0.01300	0.00061	4.7
14	0.04427	0.00033	0.7	0.04372	0.00051	1.2
15	0.01640	0.00012	0.8	0.01642	0.00032	2.0
16	0.01042	0.00055	5.2	0.01054	0.00057	5.4
17	0.00633	0.00029	4.7	0.00625	0.00022	3.5
18	0.00373	0.00020	5.4	0.00368	0.00022	6.1
19	0.00286	0.00004	1.3	0.00279	0.00004	1.3
20	0.00128	0.00006	4.7	0.00126	0.00010	7.5

Although peak height measurements are easier to make than peak area, they are much more sensitive to the particular column used. Changes in column efficiency cause variations in retention time and peak width, which affect the peak height. On the contrary, peak areas are less sensitive to these variations. In gradient elution, as the mobile phase is continuously modified, the initial condition or equilibrium state between the mobile phase and the stationary phase is not always the same at the beginning of an experiment. Generally, in this case, peak area measurements are recommended to obtain a better accuracy. However, as there are many peaks not completely resolved in the epoxy resin separation, peak height measurements give a lower standard deviation than peak area. In spite of this, peak area measurements are recommended for quantitative analysis of an epoxy resin chromatogram on a long-term basis. Comparison of results obtained with different columns or in different laboratories will be facilitated with this procedure.

3.5.4 Standard solution of acetophenone - manual injection of the sample

3.5.4.1 Preparation of the standard solution

Even if the results presented above are acceptable, direct addition of 10 μL of acetophenone with a microsyringe to the prepreg extract can produce a significant error in the amount of acetophenone. In order to improve the reproducibility of the LC method, a standard solution of acetophenone in tetrahydrofuran was prepared and an aliquot of this solution was added to the prepreg extract. The standard solution consists of 0.5 mL of acetophenone in 50 mL of THF, and each component is accurately weighed to determine the percent by weight of acetophenone (about 1.1%). A 1 mL aliquot of this solution is added to an Erlenmeyer flask, with weighing before and after to allow calculation of the exact quantity of acetophenone added (about 10.2 μg). To this is added the prepreg extract, prepared as described in Section 3.2, containing a known weight of epoxy resin. This gives a solution in which the ratio of acetophenone to epoxy resin is precisely known. Full details of the experimental procedure are given in Chapter 6.

3.5.4.2 Results based on peak area

The reproducibility of the extraction with a standard solution was checked using a Hypersil MOS-1 column. The chromatogram of the extract of Narmco 5208 prepreg, batch #1103, with the chosen baseline is shown in Figure 25. The numbering of peaks is identical to that of Figure 2.

Table 11 shows the results obtained using the normalization with acetophenone as internal standard. Peaks #12 and #13 were not well-defined, so they were not included in the calculation. A comparison with Table 8 shows a significant decrease of the relative standard deviation for the major peaks when a standard solution is employed instead of a direct addition of 10 μL of acetophenone.

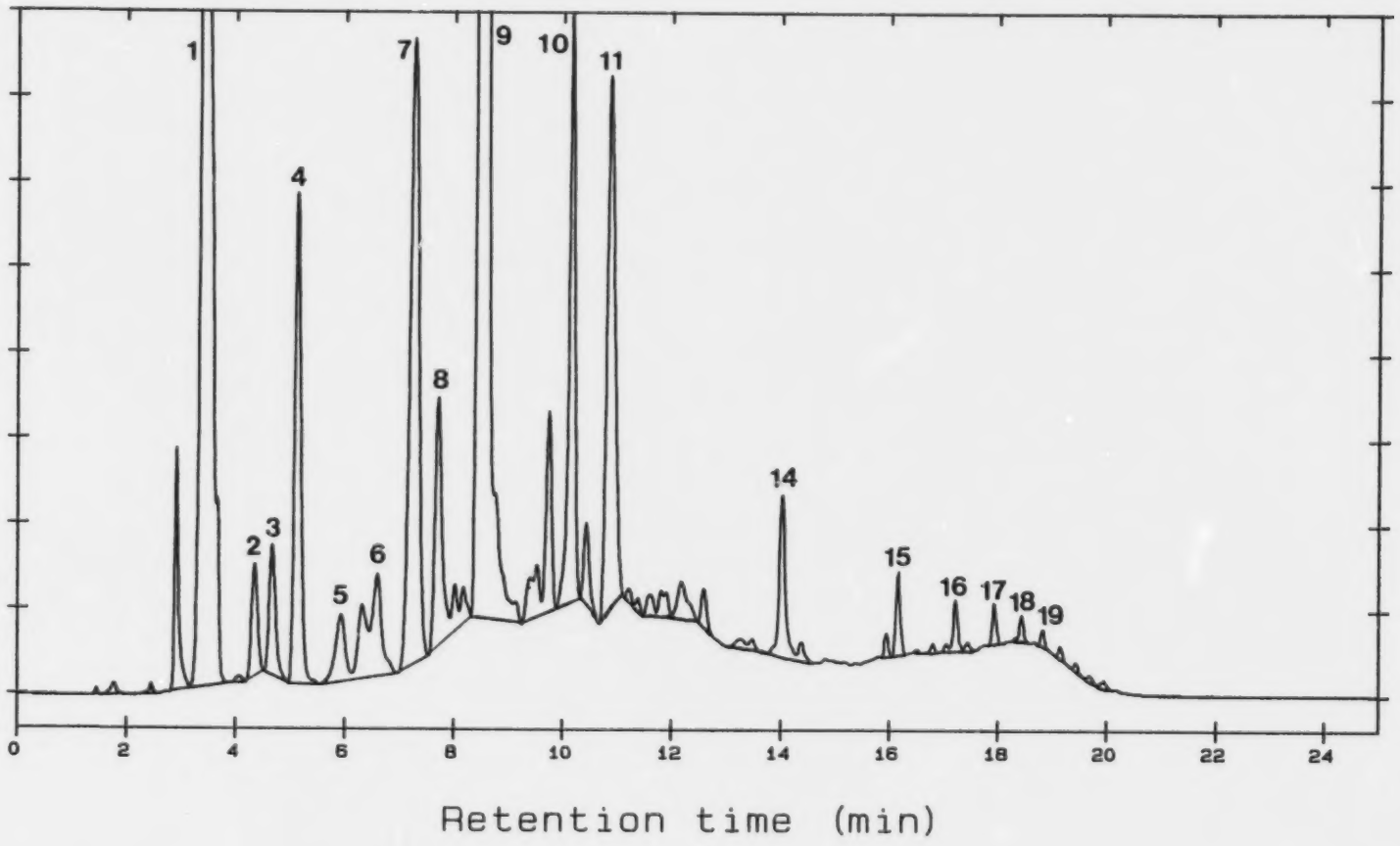


Figure 25: Drawing of the baseline on a chromatogram for quantitative measurements.
Column: Hypersil MOS-1, 25 cm X 4.6 mm i.d.

Table 11. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using normalized peak areas with respect to acetophenone internal standard; standard solution of acetophenone and manual injection.

Peak #	Average of four extractions			Average of three injections		
	Area	σ	σ (%)	Area	σ	σ (%)
1	3.43	0.16	4.7	3.373	0.060	1.8
2	0.2117	0.0031	1.5	0.2139	0.0053	2.5
5	0.2017	0.0053	2.6	0.2032	0.0078	3.8
6	0.3080	0.0051	1.6	0.3086	0.0031	1.0
7	1.738	0.020	1.1	1.734	0.014	0.8
8	0.5502	0.0040	0.7	0.5506	0.0052	0.9
9	11.98	0.10	0.8	12.02	0.12	1.0
10	1.042	0.014	1.3	1.051	0.019	1.8
11	1.335	0.013	0.9	1.342	0.010	0.8
14	0.2933	0.0048	1.6	0.2978	0.0076	2.5
15	0.1112	0.0019	1.7	0.1129	0.0024	2.1
16	0.0641	0.0029	4.4	0.2593	0.0046	1.8
17	0.0551	0.0047	8.6	0.0518	0.0013	2.4
18	0.0428	0.0029	6.7	0.0447	0.0058	12.9
19	0.0234	0.0033	14.3	0.02126	0.00016	0.8

3.5.4.3 Results based on peak height

Table 12 shows the results obtained with the peak height. In comparison with Table 9, the relative standard deviation is generally better using a standard solution of acetophenone. As in Section 3.5.3, the use of peak height measurements as detector response instead of peak area measurements gives a more precise result. This method of measurement being simpler than area measurements, it is recommended for characterizing epoxy resin prepreg when the same column is used to compare several different samples. However, injections of the same solution on different columns have shown that peak height measurements can give divergent results, even among columns with the same type of stationary phase, since the peak height is a function of the capacity factor of a solute and of the efficiency of the column. Peak area measurements, on the other hand, give similar results on different columns. Exceptions are found only for columns with a low resolution in which the superposition of many compounds leads to wrong results.

Table 12. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using normalized peak heights with respect to acetophenone internal standard; standard solution of acetophenone and manual injection.

Peak #	Average of three extractions			Average of three injections		
	Height	σ	σ (%)	Height	σ	σ (%)
1	2.074	0.063	3.0	2.0878	0.0065	0.3
2	0.2194	0.0052	2.4	0.21502	0.00069	0.3
5	0.1278	0.0019	1.5	0.1261	0.0024	1.9
6	0.1981	0.0033	1.7	0.2008	0.0041	2.1
7	1.2165	0.0041	0.3	1.212	0.028	2.3
8	0.4811	0.0015	0.3	0.4816	0.0022	0.4
9	11.720	0.025	0.2	11.696	0.015	0.1
10	1.173	0.027	2.3	1.142	0.024	2.1
11	1.047	0.011	1.0	1.0060	0.0062	0.6
14	0.3192	0.0073	2.3	0.3123	0.0094	3.0
15	0.1639	0.0036	2.2	0.16105	0.00057	0.4
16	0.0979	0.0026	2.7	0.0954	0.0048	4.9
17	0.0820	0.0025	3.1	0.0790	0.0029	3.7
18	0.0527	0.0018	3.5	0.0513	0.0011	2.1
19	0.0357	0.0011	3.0	0.03544	0.00049	1.4

3.5.4.4 Splitting of the DDS peak

The value of the normalized height for the DDS peak (#1) is substantially lower in Table 12 than in Table 9. The data in Tables 9 and 12 were obtained in September 1983 and March 1986 respectively. A period of 2.5 years separates the two analyses and the results show that the prepreg aged somewhat during this time, probably because it had been thawed several times for sampling. The values for the main epoxy TGDDM peak and the minor epoxy DGEBA peak decreased (TGDDM: 13.84 to 11.72; DGEBA: 2.09 to 1.17) and the peak of the reaction product increased (1.075 to 1.216). Since the amount of TGDDM in Narmco 5208 exceeds the amount required for stoichiometric reaction with the DDS, it is not surprising that the free DDS disappears relatively faster than the TGDDM. However, the apparent decrease in DDS is quite substantial between the two sets of measurements (10.78 to 2.07). Also, the standard deviation is worse with the Hypersil MOS-1 column than with the MCH-5-n-CAP column.

Since the efficiency of the Hypersil MOS-1 column is better than that of the MCH–5–n–CAP column, a splitting of the DDS peak was observed in some chromatograms. This is illustrated in Figure 26 for two different injections of the Narmco 5208 epoxy resin system. In the first case, there is only one peak with a small shoulder, but in the other chromatogram, two peaks are detected in addition to the shoulder. It is difficult to establish the origin of the different peaks; they may result from the presence of different isomers in the industrial hardener. As the separation with the MCH-5-n-CAP column is not good enough to separate these isomers, this phenomenon was not observed before.

This result underlines one of the main problems of gradient elution, namely the regeneration of the column. The splitting of the DDS peak is not always present and this is attributed to the initial condition of the column. If, for some reason, the equilibrium between the stationary phase and the mobile phase is not always identical, certain experimental conditions can favour the separation of DDS components whereas in other conditions, isomers will be completely unresolved.

The splitting of the peak influences the peak height and hence the normalized height. The major DDS peak seems to be the first one and the height of this peak was used for calculation. Thus, a column with excellent resolution has some advantages but it must be used with circumspection in the case of the DDS peak. For quantitative measurement, it is advisable to calculate the normalized area using the combined area of these peaks since these compounds are included in the single peak of DDS when the separation is not complete.

3.5.5 Standard solution of acetophenone - automatic injection of the sample

In order to check the influence of the manual injection, a set of chromatograms was obtained with an autosampler. The results are given only for the normalized area (Table 13) and normalized height (Table 14). The relative standard deviation did not significantly decrease with the autosampler, indicating that the main variation arises from the extraction process.

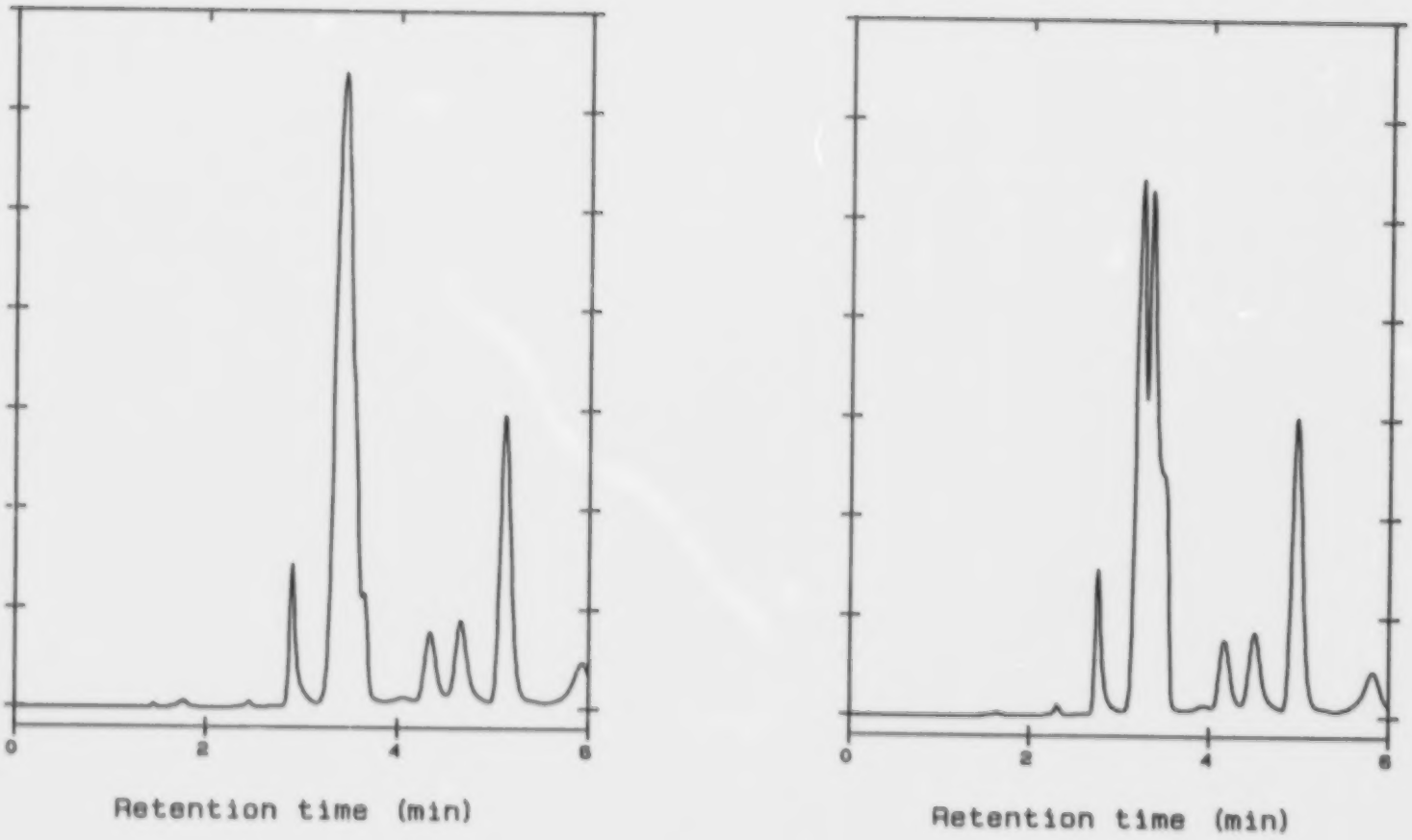


Figure 26: RPLC separation of Hardener HT 976 in THF.
Column: Hypersil MOS-1, 25 cm X 4.0 mm i.d.

Table 13. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using normalized peak areas with respect to acetophenone internal standard; standard solution of acetophenone and automatic injection.

Peak #	Average of four extractions			Average of three injections		
	Area	σ	σ (%)	Area	σ	σ (%)
1	3.677	0.094	2.5	3.5829	0.0060	0.2
2	0.2200	0.0054	2.5	0.21564	0.00036	0.2
5	0.2078	0.0086	4.1	0.196	0.017	8.7
6	0.3253	0.0083	2.6	0.318	0.011	3.6
7	1.770	0.033	1.9	1.7598	0.0016	0.1
8	0.5540	0.0057	1.0	0.5601	0.0016	0.3
9	12.08	0.16	1.3	11.953	0.015	0.1
10	1.081	0.033	3.0	1.0517	0.0012	0.1
11	1.353	0.018	1.3	1.3385	0.0016	0.1
14	0.276	0.040	14.6	0.2881	0.0016	0.6
15	0.1135	0.0042	3.7	0.10937	0.00067	0.6
16	0.0669	0.0054	8.0	0.06187	0.00044	0.7
17	0.0547	0.0044	8.1	0.05061	0.00046	0.9
18	0.03928	0.00071	1.8	0.0396	0.0040	10.0
19	0.02134	0.00071	3.3	0.02071	0.00087	4.2

Table 14. RPLC results for Narmco 5208 prepreg, batch #1103, calculated using normalized peak heights with respect to acetophenone internal standard; standard solution of acetophenone and automatic injection.

Peak #	Average of four extractions			Average of three injections		
	Height	σ	σ (%)	Height	σ	σ (%)
1	1.90	0.30	15.8	1.846	0.086	4.7
2	0.2302	0.0064	2.8	0.22559	0.00097	0.4
5	0.1305	0.0031	2.4	0.1271	0.0056	4.4
6	0.204	0.011	5.2	0.2171	0.0041	1.9
7	1.269	0.031	2.5	1.307	0.025	1.9
8	0.482	0.011	2.2	0.497	0.015	0.3
9	11.84	0.21	1.8	11.944	0.036	0.3
10	1.229	0.049	4.0	1.193	0.030	2.5
11	1.082	0.013	1.2	1.083	0.010	1.0
14	0.305	0.046	14.9	0.319	0.012	3.9
15	0.1669	0.0043	2.6	0.1628	0.0024	1.5
16	0.1026	0.0035	3.4	0.0994	0.0054	5.5
17	0.0864	0.0020	2.3	0.0844	0.0038	4.5
18	0.05285	0.00040	0.8	0.05233	0.00038	0.7
19	0.03654	0.00094	2.6	0.03593	0.00080	2.2

Since tetrahydrofuran is rather volatile, its use can lead to error during sample manipulation. In order to minimize this error, an experiment was done in which tetrahydrofuran was replaced by dioxane. Although evaporation losses were lower with dioxane, the final reproducibility with respect to different extractions of the prepreg was worse than with THF. Thus, in spite of its volatility, THF is the best choice for chromatographic analysis.

3.6 Comparison of different batches of Narmco 5208 resin

Different batches of the Narmco Rigidite 5208 epoxy resin system were analysed by RPLC according to the method described in Chapter 6. They included five prepregs (batches #1101, #1103, #1104, #1010, #1014), the neat resin on a plastic backing sheet (batch #1047) and the neat resin in bulk form (batch #1023). Resins were dissolved in tetrahydrofuran and injected, after filtration, on an MCH-5-n-CAP column, 30 cm long x 4.0 mm i.d.. For each batch, two solutions or extractions were prepared except for batch #1014 which was extracted four times. Each solution was injected three times and the averages of all these values are reported in Table 15 (area) and in Table 16 (height). The peak numbering is consistent with Figure 2. The results are reported as normalized values with respect to acetophenone internal standard. In addition, ratios with respect to the TGDDM peak are reported for the main peaks of interest. These ratios are independent of the presence of acetophenone. A computer malfunction resulted in the loss of the data for batch #1103 before the areas were calculated, so this batch is missing from Table 15.

Appreciable variations can be observed among the different batches. For example, peak #9, corresponding to the main epoxy monomer TGDDM, varies significantly from batch to batch. Batch #1047 is the least advanced since the values for free TGDDM and DDS (peak #1) are the highest. This is confirmed by the low value for peak #7, which is the product of the reaction between TGDDM and DDS. However, the content of free DGEBA (peak #10, from the Novolac) is abnormally low compared to the other batches. Thus, it appears that this batch is unbalanced with respect to the usual composition. Batch #1023 lies at the other extreme, having the lowest values for free TGDDM, DDS, and DGEBA, and the highest value for the reaction product. Although it consists of neat resin, it is more advanced than all the prepreg samples, probably the result of undue heating at some point in its history.

Table 15. RPLC results for different batches of the Narmco 5208 system; normalized areas with respect to acetophenone, and area ratios w. r. t. TGDDM

Peak	1101	1104	1010	1014	1047	1023
1 (DDS)	3.600	4.311	3.719	4.130	4.795	3.034
2	0.221	0.253	0.262	0.255	0.215	0.237
3	0.141	0.148	0.200	0.129	0.141	0.225
5	0.127	0.115	0.125	0.146	0.131	0.086
6	0.332	0.206	0.303	0.217	0.296	0.429
7 (RP)	1.742	1.336	1.785	1.623	1.110	2.406
8	0.612	0.690	0.638	0.831	0.836	0.830
9 (TGDDM)	12.72	13.19	12.70	13.37	13.54	12.33
10 (DGEBA)	1.324	1.626	1.185	1.552	0.792	0.709
11	1.474	1.899	0.668	---	0.898	0.567
13	0.287	0.379	0.272	0.418	0.141	0.131
14	0.211	0.309	0.241	0.250	0.342	0.243
15	0.087	0.119	0.114	0.138	0.036	0.014
16	0.082	0.101	0.107	0.127	0.136	0.026
1/9	0.283	0.327	0.293	0.309	0.354	0.246
7/9	0.137	0.101	0.141	0.121	0.082	0.195
10/9	0.104	0.123	0.093	0.116	0.058	0.057

Table 16. RPLC results for different batches of the Narmco 5208 system; normalized heights with respect to acetophenone, and height ratios w. r. t. TGDDM

Peak	1103	1101	1104	1010	1014	1047	1023
1 (DDS)	7.229	6.717	8.088	6.816	7.495	9.398	5.966
2	0.191	0.178	0.204	0.179	0.197	0.224	0.176
3	0.092	0.104	0.099	0.110	0.088	0.152	0.156
5	0.108	0.135	0.128	0.142	0.157	0.146	0.076
6	0.258	0.319	0.196	0.293	0.205	0.138	0.445
7 (RP)	1.347	1.501	1.155	1.527	1.308	0.981	2.165
8	0.575	0.642	0.656	0.639	0.705	0.707	0.666
9 (TGDDM)	12.46	13.06	13.48	12.94	13.51	14.34	12.84
10 (DGEBA)	1.607	1.226	1.579	1.374	1.931	0.895	0.756
11	1.061	0.882	1.163	0.639	0.608	0.764	0.551
13	0.415	0.300	0.405	0.370	0.471	0.128	0.108
14	0.394	0.300	0.411	0.300	0.371	0.347	0.267
15	0.186	0.140	0.192	0.179	0.217	0.058	
16	0.115	0.090	0.121	0.118	0.144	0.028	
1/9	0.580	0.514	0.600	0.527	0.555	0.655	0.465
7/9	0.108	0.115	0.086	0.118	0.097	0.068	0.169
10/9	0.129	0.094	0.117	0.106	0.143	0.062	0.059

Comparison of the five prepreg samples shows results which are in better agreement. Generally speaking, batches #1010 and #1101 are very similar to each other, while the other three (#1014, #1103, and #1104) are also similar to each other but less advanced than the first two. Using the reaction product peak (#7) as a criterion, all seven batches may be arranged in the following order as to "degree of advancement": 1023 > 1010 ≈ 1101 > 1014 ≈ 1103 > 1104 > 1047. The relationships between some of the main peaks are shown graphically in Figures 27 to 29, where the normalized peak heights for the reaction product, DGEBA, and TGDDM are plotted against those of DDS. There are obvious correlations. In general, a decrease in free DDS correlates with a decrease in TGDDM and DGEBA and an increase in reaction product, as expected based on the nature of the curing reaction. These results indicate that the batches differ mainly in degree of reaction advancement and not in initial composition. One exception is batch #1047, which deviates considerably from the linear relationship in some cases (notably Figure 28). This batch is believed to have an unusually low Novolac content.

The same trends are evident whether the normalized peak intensities or the peak ratios are used as an indicator. However, the normalized peak intensities provide a more complete picture of the variations in composition.

3.7 Calibration curves

In order to evaluate the percentages of the two epoxy resins and the hardener in Narmco 5208, calibration curves were determined for the individual components Hardener HT 976, Araldite MY 720, and Epi-Rez SU-8. For each component, several THF solutions were prepared containing a known concentration of acetophenone and varying known concentrations of the particular component. For each solution, the RPLC chromatogram was measured, and a response R calculated based on the main peak (DDS, TGDDM, or DGEBA, depending on the component). This response, given by:

$$\text{Response R} = \text{Peak height} + \left[\frac{\text{Acetophenone peak height}}{\text{Acetophenone concentration (wt \%)}} \right]$$

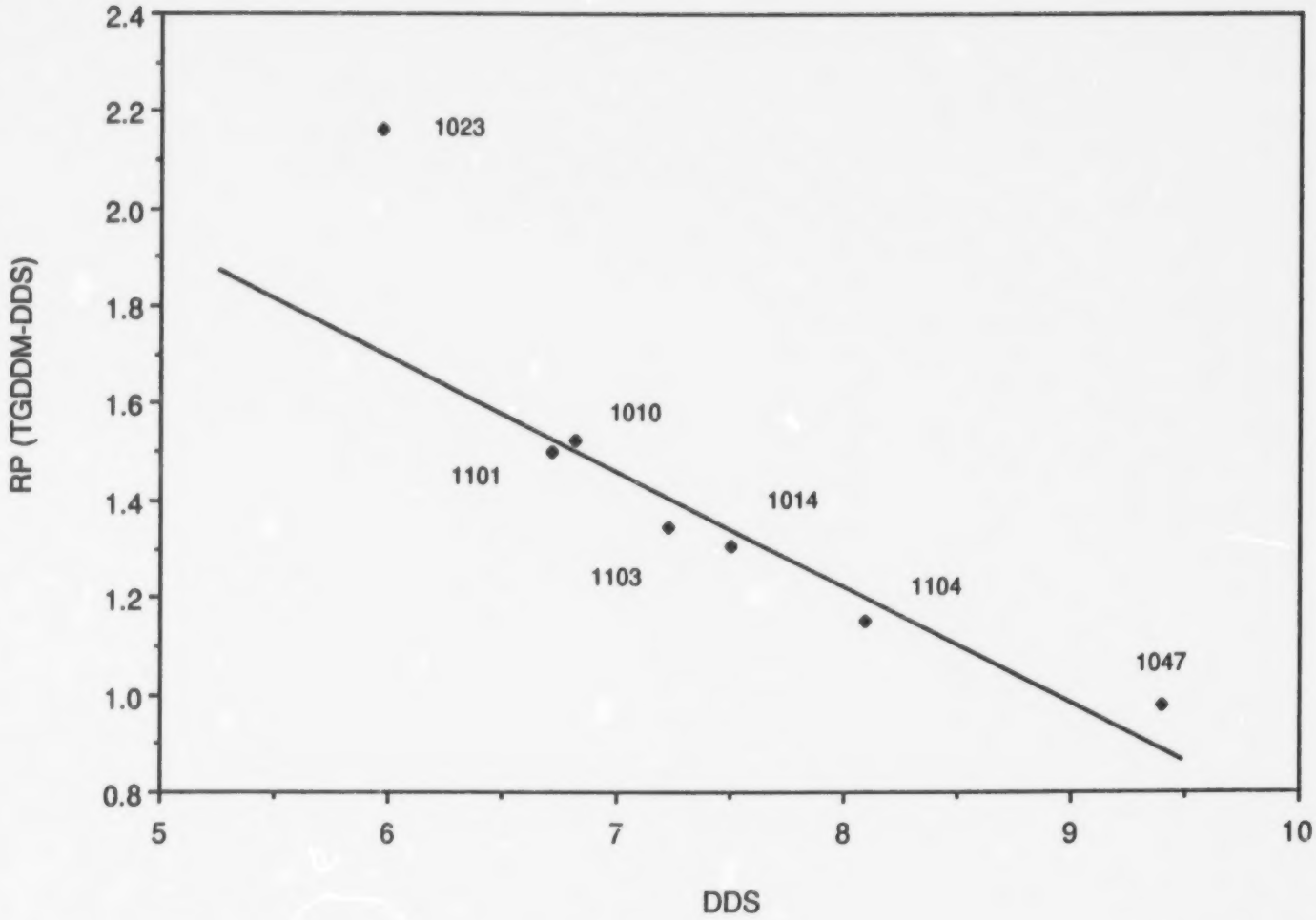


Figure 27: Variation of the normalized peak height of the reaction product as a function of the normalized peak height of DDS.

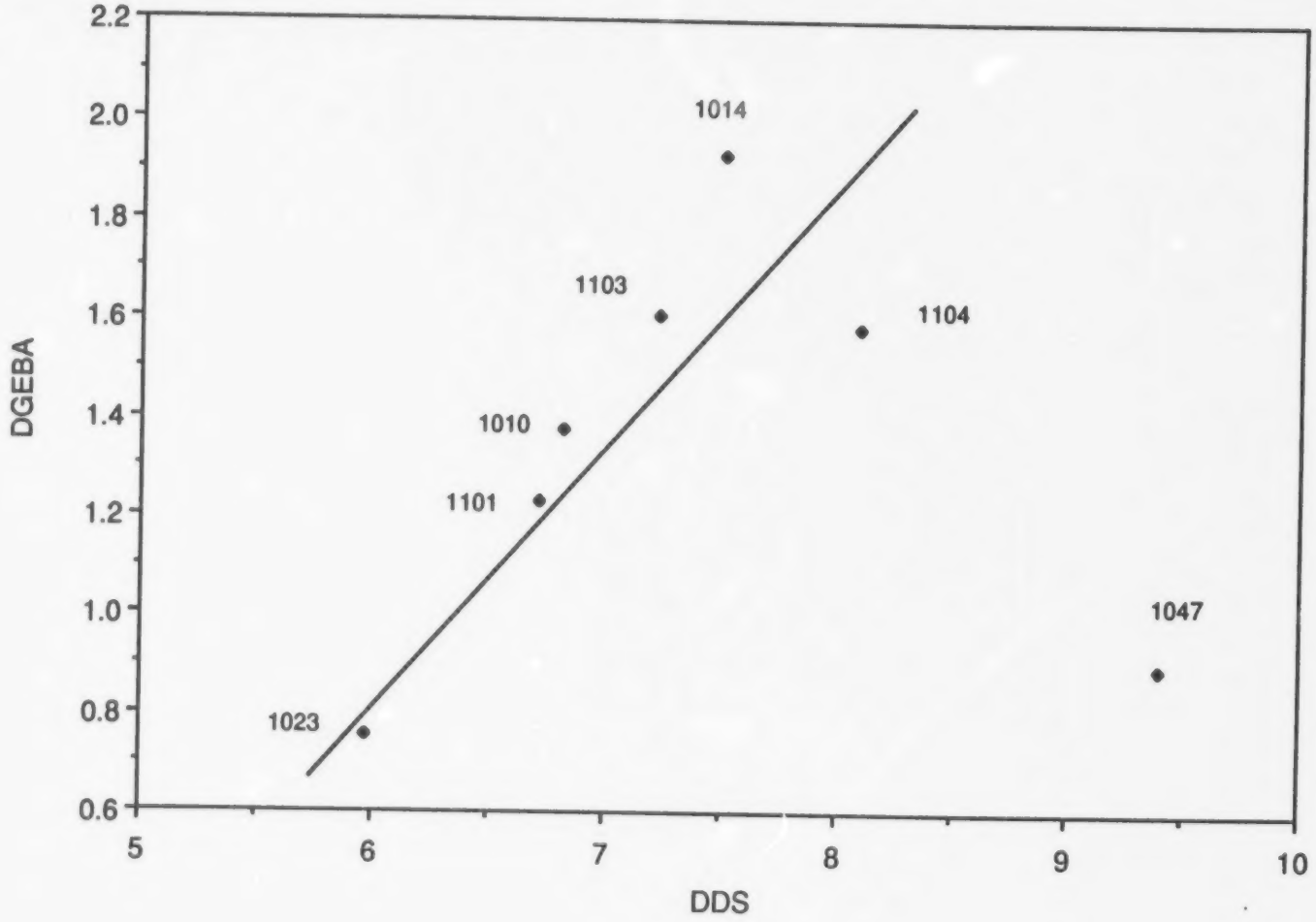


Figure 28: Variation of the normalized peak height of DGEBA monomer as a function of the normalized peak height of DDS.

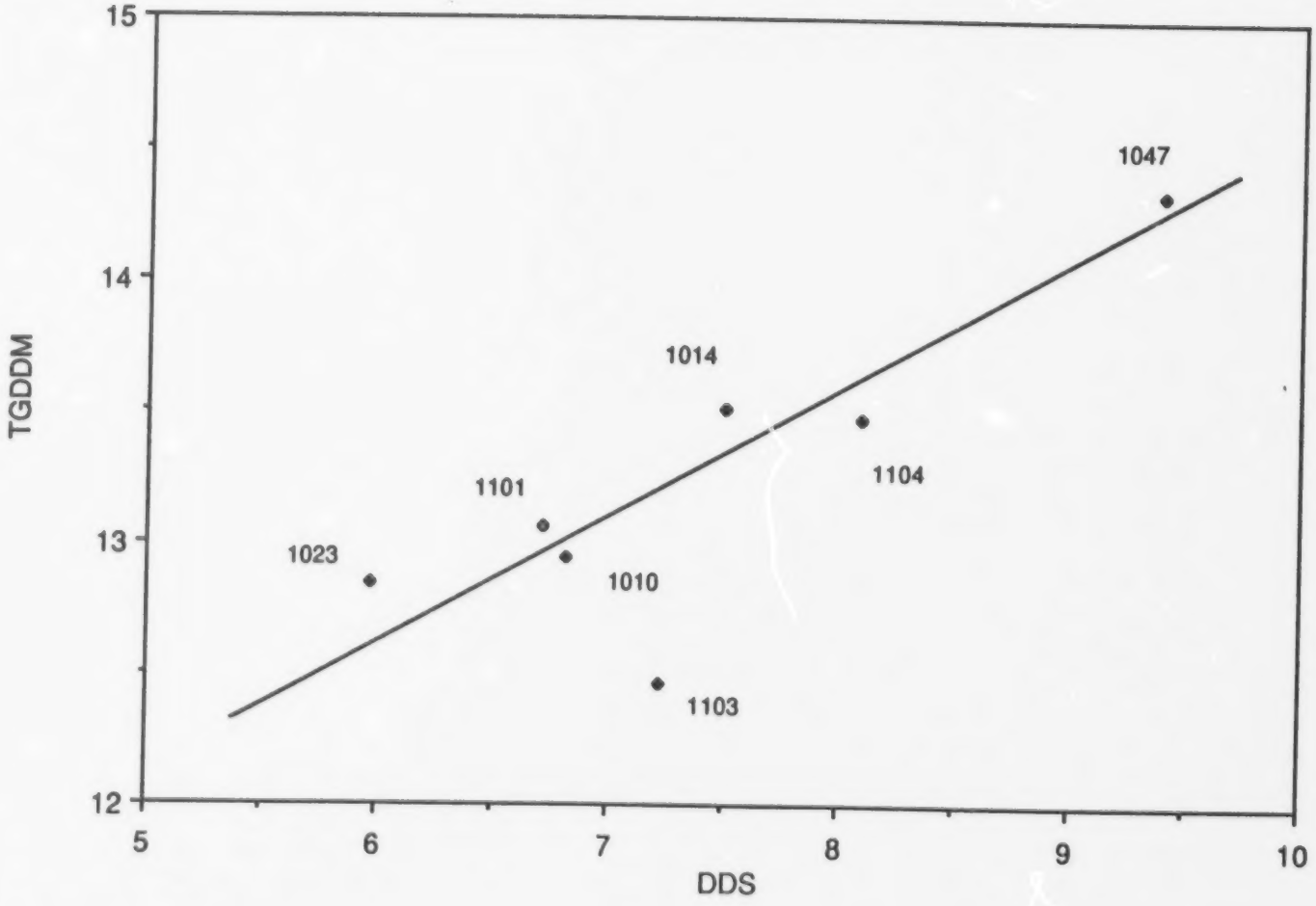


Figure 29: Variation of the normalized peak height of TGDDM monomer as a function of the normalized peak height of DDS.

is directly related to the concentration of the component in question, P (wt %). For each one, a linear relation was found:

Hardener HT 976:	R = 0.2705 x P - 0.00054
Araldite My 720:	R = 0.2047 x P + 0.0109
Epi-Rez SU-8:	R = 0.1445 x P - 0.00044

The squared correlation coefficient was greater than 99% in all cases. To estimate the percentage of each component in a sample of Narmco 5208, we prepare a solution containing known concentrations of resin and acetophenone, measure the RPLC chromatogram, determine the peak height of the compound of interest, calculate the response and hence the concentration associated with this value, and divide it by the overall resin concentration to find the percentage of the particular component in the resin. The calculation is somewhat approximate since it is based on only the major peak of each component, and it assumes that each component in the epoxy mixture has the same composition as the product used for calibration. It should be noted that the percentages determined correspond to unreacted material, so the sum will be less than 100% if the resin is advanced.

Table 17 reports values for some batches. The results are similar to those reported in the literature. However, some caution must be exercised for the HT 976 (DDS) because of the splitting sometimes observed with this peak, which can influence the measured amount. In batch #1047, the low value observed for the Novolac, together with a "normal" value for MY 720 and a high value for HT 976, indicates that the batch was made with a low content of Novolac. In batch #1023, however, the low value for the Novolac is more probably due to a high degree of advancement, since the HT 976 value is also low and the sum of the three is only 83%.

Table 17. Percentage (by weight) of each component in some batches of Narmco 5208 epoxy resin.

Batch	HT 976	MY 720	Novolac	Sum
1103	26.83 ± 0.02	55.8 ± 0.4	11.74 ± 0.09	94.4
1014	27.7 ± 0.3	60.5 ± 0.7	13.76	102.0
1047	34 ± 1	54 ± 1	7.0 ± 0.1	95
1023	22.4 ± 0.3	55 ± 1	5.69 ± 0.05	83
ref.12	23.6	64.2	10.1	97.9

3.8 Effect of heating on the prepreg

In order to confirm the location of the reaction product peak, a Narmco 5208 prepreg, batch #1014, was heated at 100°C for 0, 0.5, 1.0, 2.0, 3.0, and 4.0 hours. The separation was achieved on a Hypersil MOS-1 column, 25 cm long x 4.6 mm i.d., using the experimental conditions described in Section 3.3. The percentages of resin extracted from the samples were as follows: 41.11%, 41.27%, 41.14%, 40.84%, 40.08%, and 40.71%. Figure 30 shows the chromatograms obtained for no heating and 4 hours of heating. The normalized peak heights were calculated and are reported in Table 18. Figures 31 to 33 show the variation of some peaks as a function of the heating time.

Table 18. Effect of heating at 100°C on Narmco 5208 prepreg, batch #1014, Hypersil MOS-1 column.

	0 h	0.5 h	1.0 h	2.0 h	3.0 h	4.0 h
1 (DDS)	1.565	1.912	1.694	1.353	1.388	1.170
2	0.205	0.193	0.186	0.167	0.158	0.143
5	0.186	0.183	0.182	0.168	0.164	0.156
6	0.276	0.242	0.261	0.256	0.253	0.243
7 (RP)	1.442	1.495	1.550	1.608	1.661	1.651
8	0.532	0.535	0.544	0.534	0.531	0.521
9 (TGDDM)	12.885	11.730	11.751	11.278	11.005	10.597
10 (DGEBA)	1.329	1.255	1.173	1.079	1.052	0.958
11	0.675	0.634	0.591	0.541	0.517	0.473
14	0.343	0.317	0.288	0.255	0.244	0.214
15	0.172	0.157	0.144	0.128	0.122	0.104
16	0.105	0.103	0.090	0.080	0.084	0.075
17	0.086	0.090	0.088	0.074	0.078	0.066
18	0.063	0.054	0.046	0.046	0.041	0.031
19	0.039	0.034	0.032	0.028	0.027	0.026

Only peak #7 increased with time. With information obtained from the IR spectrum (Section 3.4.2), it was confirmed that this peak corresponds to the reaction product. After a certain time, the quantity tends to stabilize because this molecule (DDS-TGDDM) continues to react with other molecules to form the polymer. At the same time, the quantities of DDS and DGEBA (Figure 31) and TGDDM (Figure 32) continue to decrease with the heating time indicating a further reaction of these species. It is interesting to note the decrease of the peaks which appear at the end of the chromatogram (peaks #16, #17,

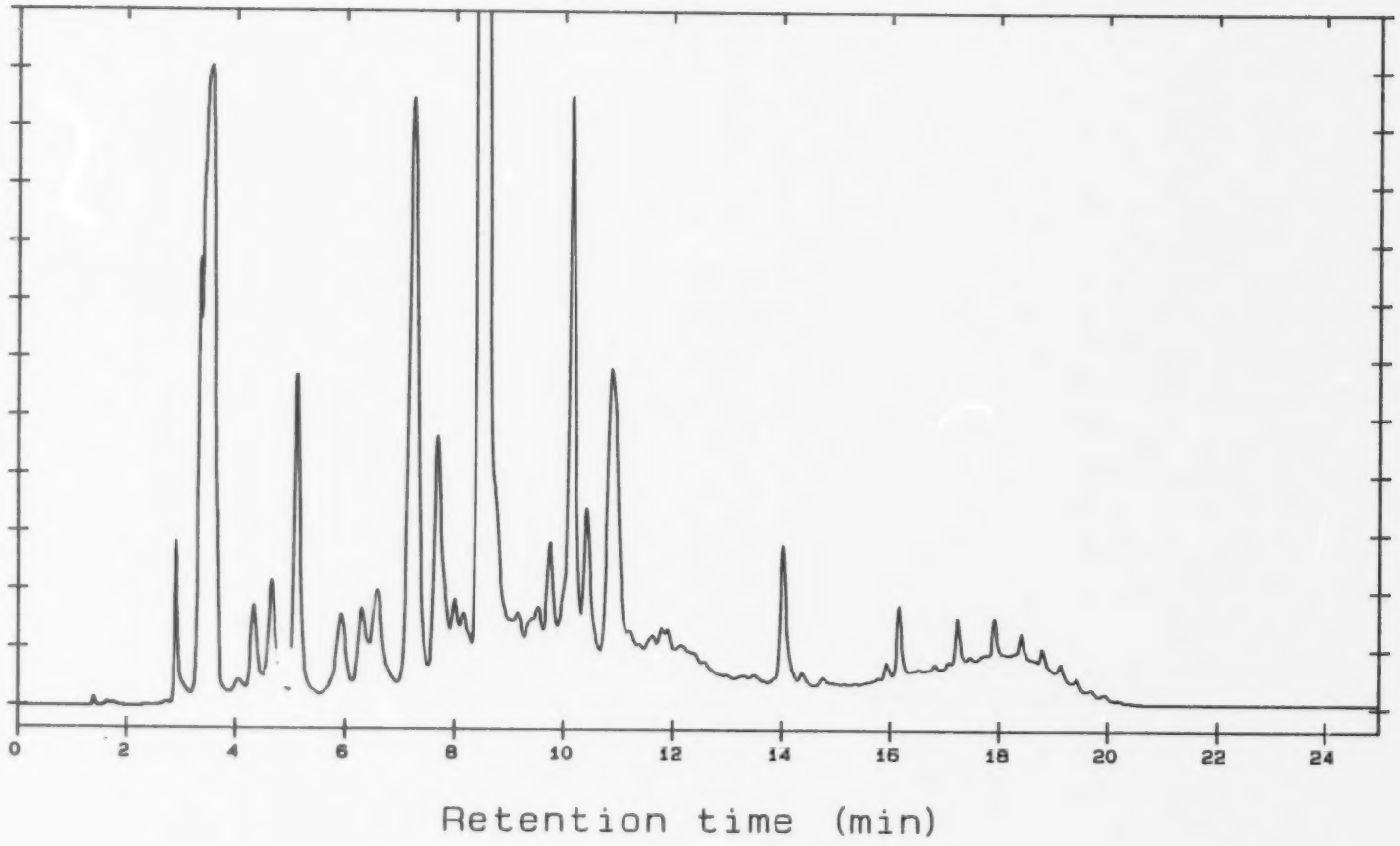


Figure 30a: RPLC separation of the extract of Narmco 5208 prepreg, batch #1014.
Column: Hypersil MOS-1, 25 cm X 4.6 mm i.d..
No heating.

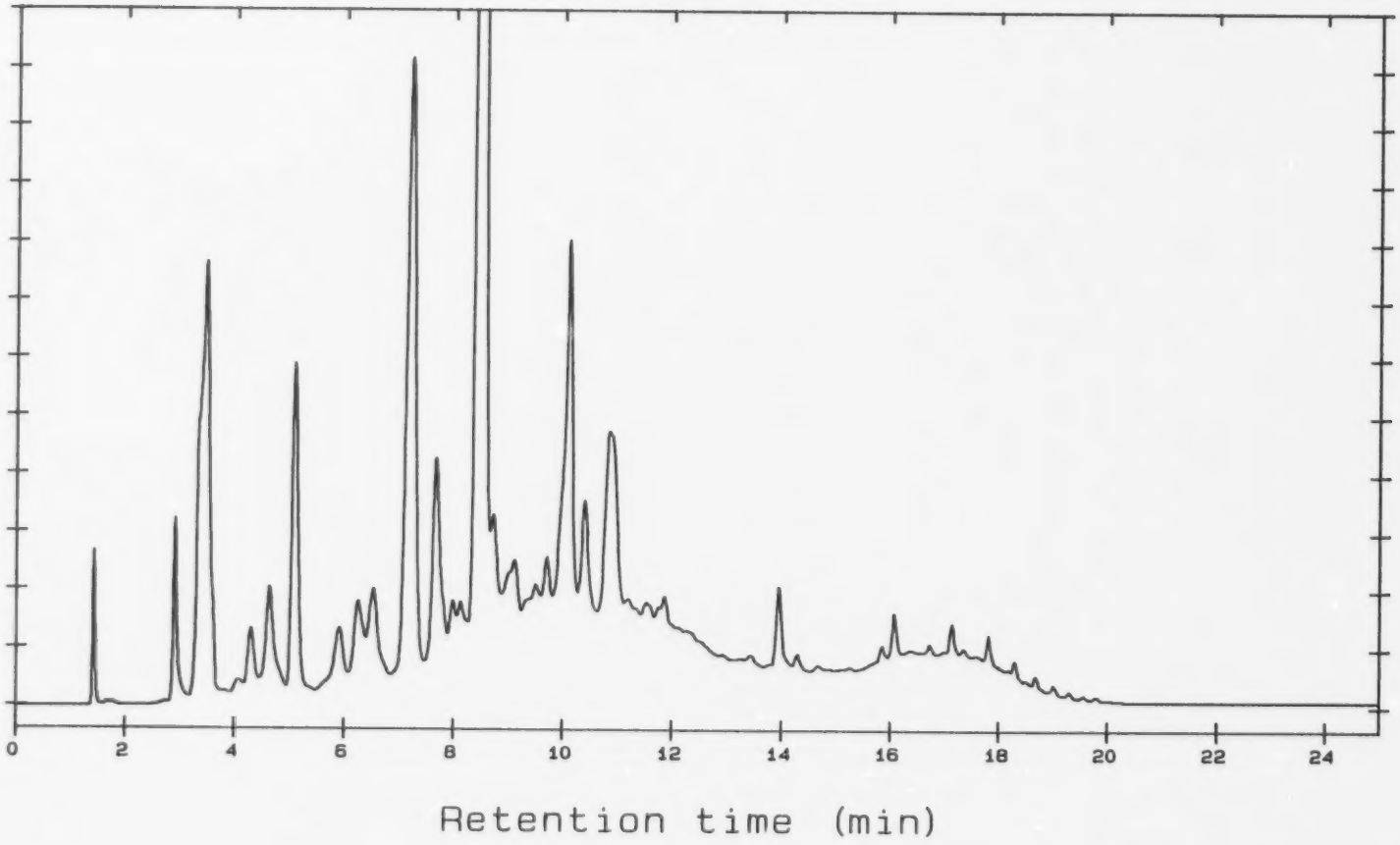


Figure 30b: RPLC separation of the extract of Narmco 5208 prepreg, batch #1014.
Column: Hypersil MOS-1, 25 cm X 4.6 mm i.d..
Heating 4 hours at 100°C.

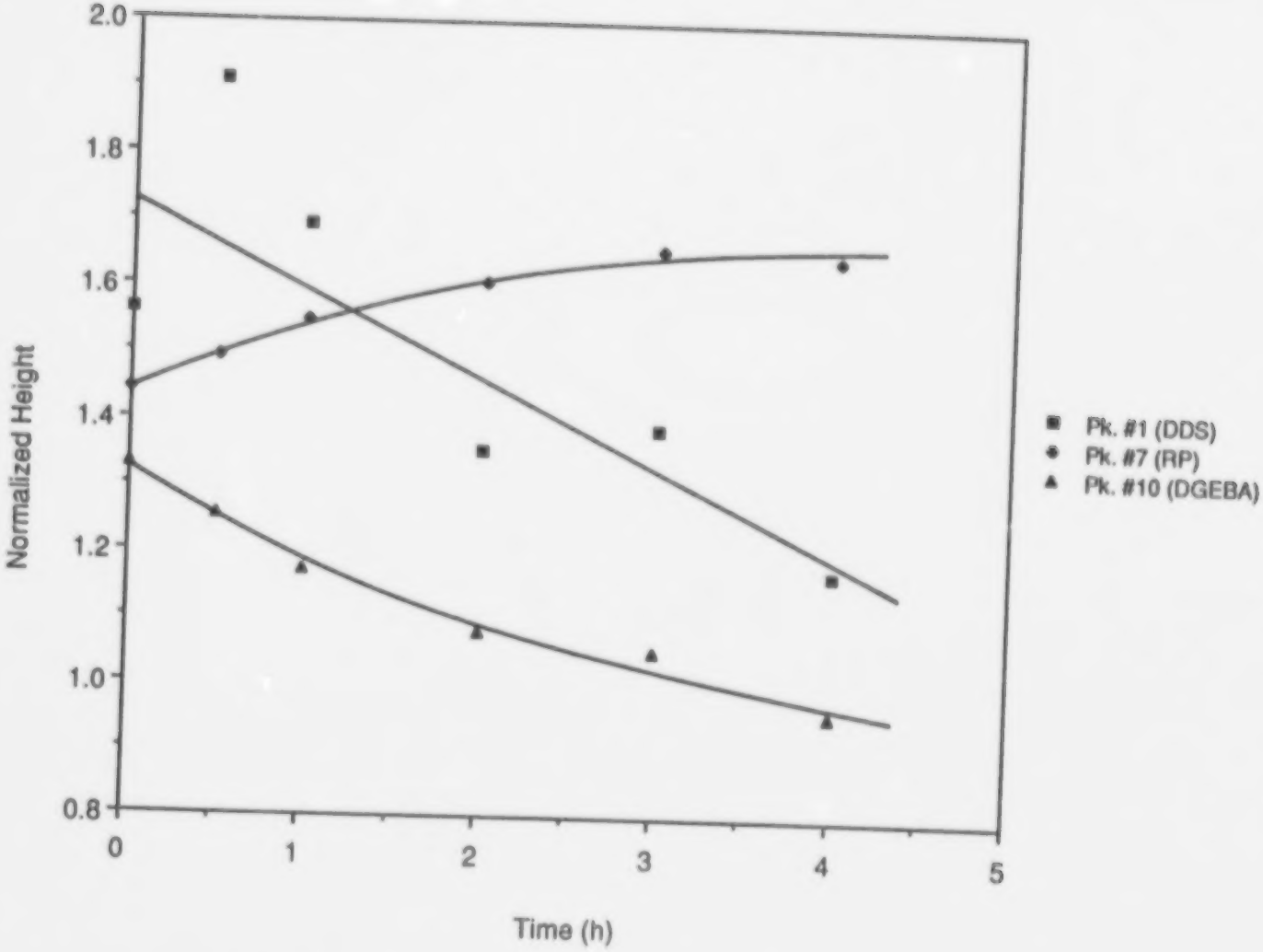


Figure 31: Variation of the normalized peak height as a function of the curing time for peaks #1, #7 and #10.

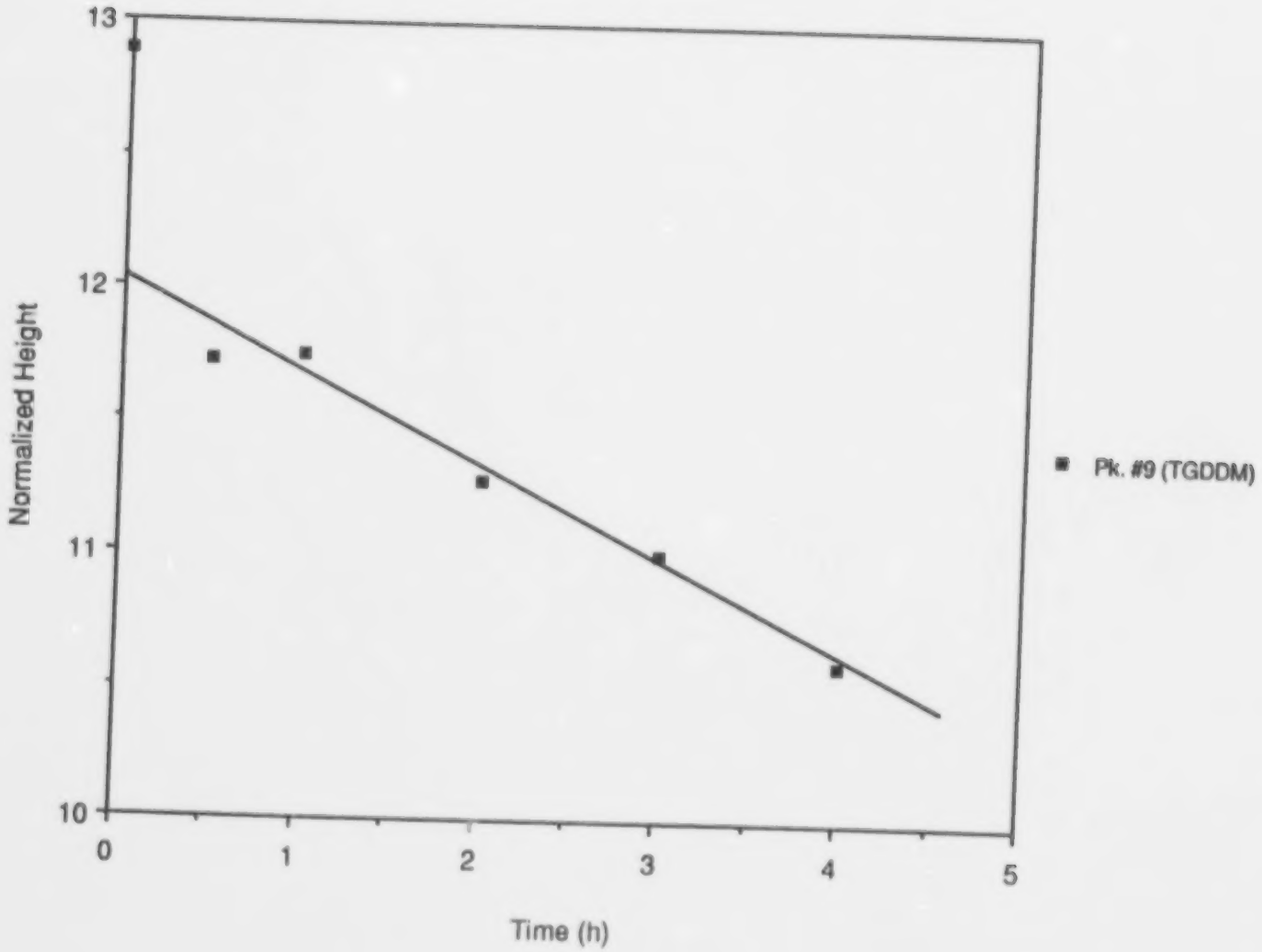


Figure 32: Variation of the normalized peak height as a function of the curing time for peak #9.

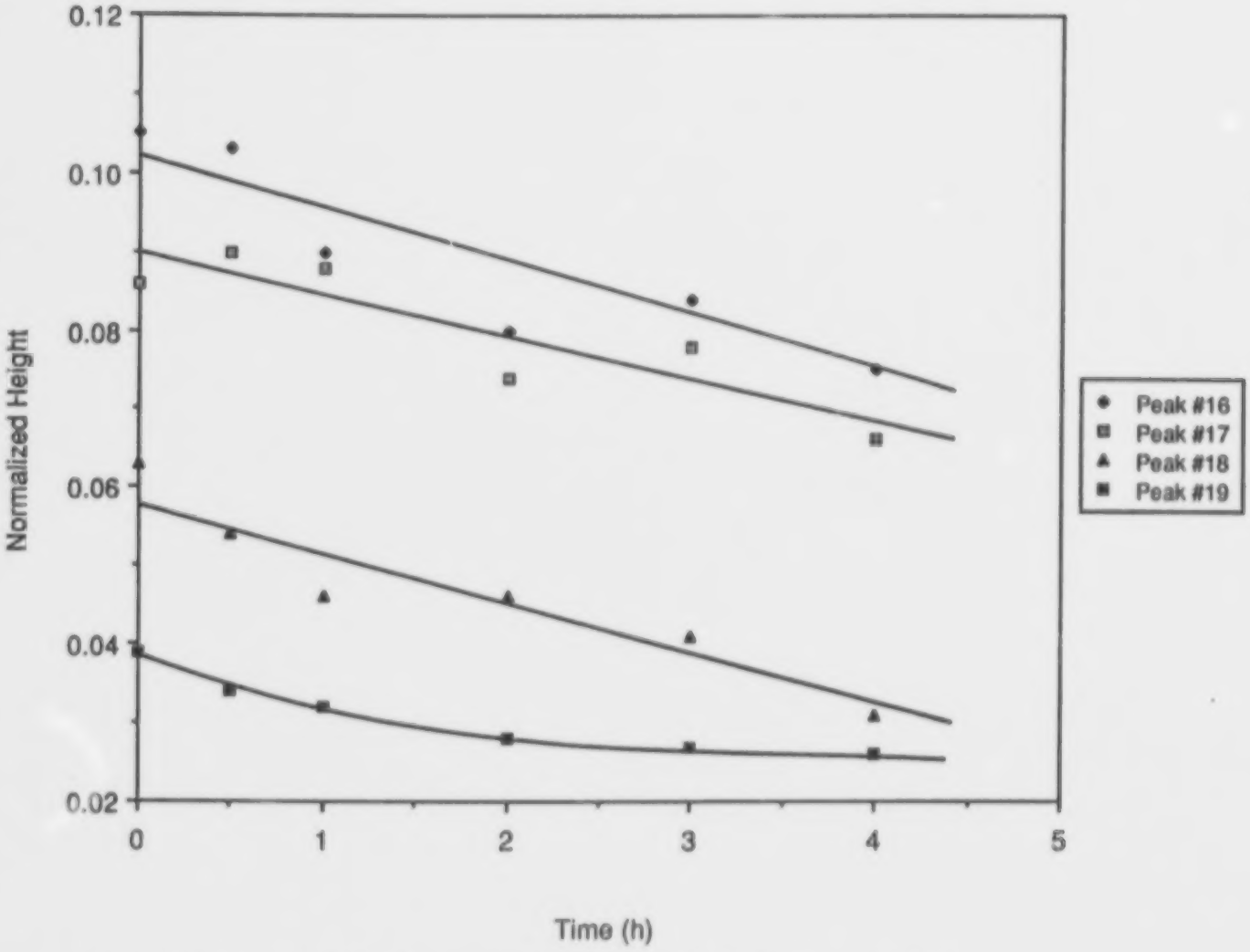


Figure 33: Variation of the normalized peak height as a function of the curing time for peak #16, #17, #18 and #19.

#18, #19; Figure 33). These belong to the Novolac resin and are probably oligomers. According to Seferis [12,13], the Novolac reacts faster than the TGDDM with the DDS.

Peak #6, which is not found in any of the three starting products, is relatively stable, indicating that it is not a reaction product. Comparison of the chromatograms (Figure 30) shows that a peak eluting just after the TGDDM peak increases with time. This is possibly a combination of one DDS molecule with one molecule of DGEBA, but this has not been confirmed. In addition, as this peak is not well resolved, it is not recommended to use it to follow the advancement of the reaction.

To conclude, peak #7 has been formally identified as the peak of the reaction product between the main epoxy TGDDM and the hardener DDS, and it is a good indication of the degree of advancement of the epoxy resin.

3.9 Effect of water and nitric acid on Araldite MY 720

The effect of water and nitric acid on a solution of epoxy resin Araldite MY 720 was examined in order to locate the peaks in the chromatogram corresponding to the various glycols created by the opening of epoxy rings. Solutions of about 0.25% by weight of MY 720 were made up in THF, in a binary mixture THF/H_2O (50:50), and in THF/0.001 M HNO_3 (50:50). Chromatograms of these mixtures were measuredon a Hypersil ODS column, 25 cm long x 4.6 mm i.d., at regular intervals over a period of about 150 hours. The results presented here are preliminary and have not been repeated; they are given only as an indication.

Figure 34 shows chromatograms of the epoxy resin in THF after 3.5 hours and 142 hours. There is no substantial change in the chromatogram. The main peak (TGDDM) decreased slightly and a shoulder appeared on the peak labeled A.

Figure 35 shows chromatograms of MY 720 in the binary mixture THF/H_2O (50:50) at 2.5 hours, 47 hours, and 141 hours. A small peak appears at the same location as the peak of acetophenone. In this case also there is a small decrease of the TGDDM peak. A comparison of this chromatogram with the results of Pearce [14] suggests that this small peak can be related to the opening of the epoxy ring to form a glycol. However, a formal identification of this peak has not been made.

In order to accelerate the formation of glycol, a 50:50 mixture THF/0.001 M HNO_3 was used. Chromatograms of the Araldite MY 720 after 1.4 and 140 hours are given in Figure 36. After 140 hours, a larger peak appeared at the same retention time as acetophenone (shoulder) and the peak before the acetophenone increased significantly. In

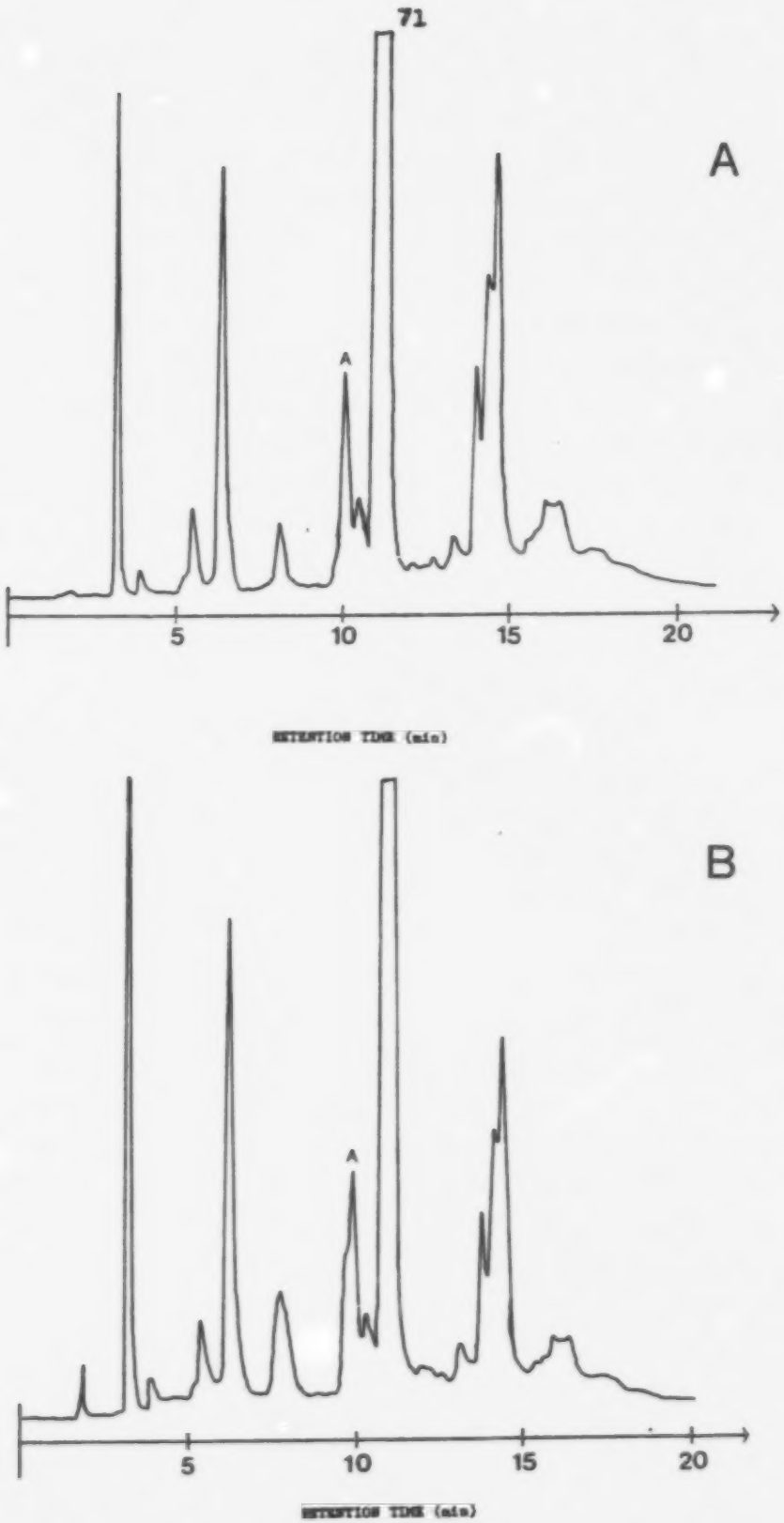


Figure 34: RPLC separation of a solution of Araldite MY 720 in THF after (A) 3.5 h and (B) 142 h.
Column: Hypersil ODS, 25 cm X 4.6 mm i.d..

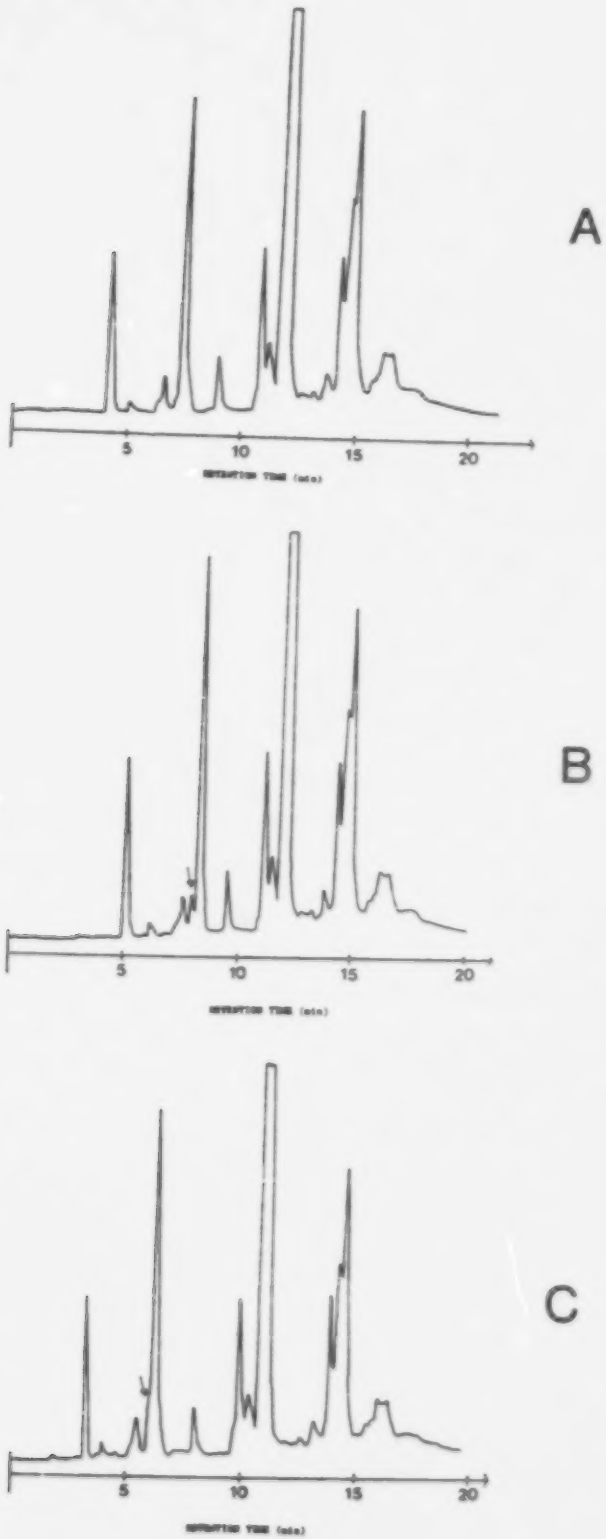


Figure 35: RPLC separation of a solution of Araldite MY 720 in a binary mixture THF/H20 (50:50) after (A) 2.5 h, (B) 47 h and (C) 141 h. Column: Hypersil ODS, 25 cm × 4.6 mm i.d..

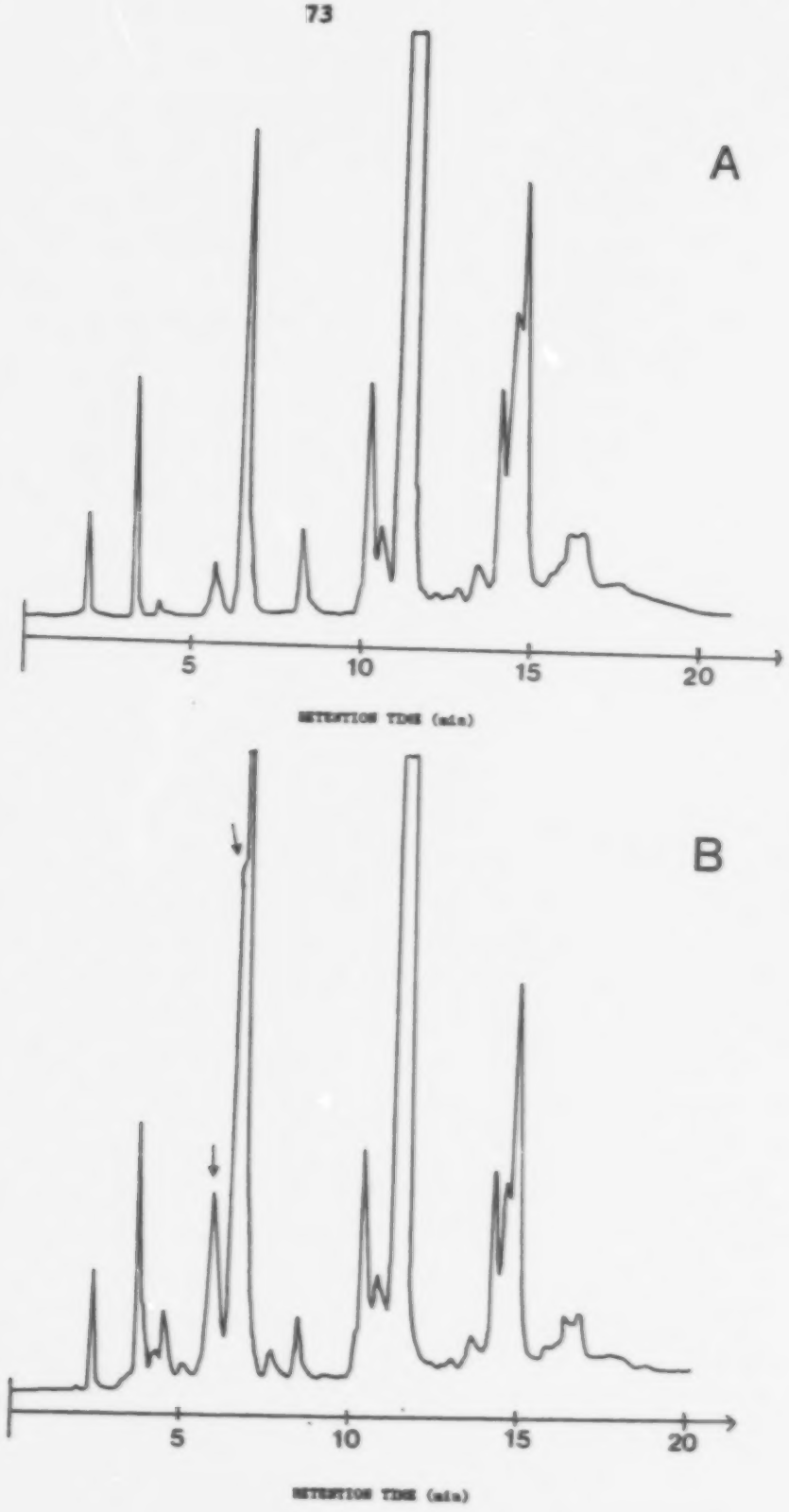


Figure 36: RPLC separation of a solution of Araldite MY 720 in a mixture THF/0.001 M HNO_3 after (A) 1.4 h and (B) 140 h. Column: Hypersil ODS, 25 cm X 4.6 mm i.d..

addition, small peaks appeared around 3-4 minutes. They are probably related to the nitration of the TGDDM. A more advanced solution (without acetophenone) shows the increase of these peaks (Figure 37). The nitration of TGDDM gives a product with an absorbance maximum around 610 nm [15]. The chromatogram at 610 nm shows small peaks only in this region, confirming the presence of nitrated product.

Peak #4 in Figure 37 was collected and analysed by diffuse reflectance infrared spectroscopy. The spectrum is given in Figure 38. A subtraction of the IR spectrum of the TGDDM peak (peak #9, Figure 2) gives the spectrum represented in Figure 39. The appearance of alcohol bands (1120 cm^{-1}, secondary OH; 1050 cm^{-1}, primary OH) and the decrease of the epoxy C-H bands near 3000 cm^{-1} are indicative of the conversion of epoxy rings to glycol. For this peak, the ratio of the area of the epoxy bands between 1000 and 900 cm^{-1} against that of the aromatic band (1510 cm^{-1}) gives a value of 0.19, whereas the same ratio is 0.38 for pure TGDDM (peak #9). This suggests that the peak corresponds to a molecule of TGDDM in which two of the four epoxy rings are opened. It is possible that peak #5 corresponds to a molecule in which only one ring is opened. However, these hypotheses need to be confirmed by other experiments.

In conclusion, the "glycol peak" does not appear to be particularly important in the case of TGDDM, since it was not detected unless acid was used to accelerate its formation.

3.10 Conclusion

Reverse-phase liquid chromatography is an excellent technique for analysing epoxy resin systems such as Narmco 5208. The separation has been optimized by using a gradient elution method with acetonitrile-water with UV detection at 230 nm. The addition of acetophenone as an internal standard permits accurate quantitative analysis using a normalization of the peak area or peak height with respect to the weight of the extracted resin and the weight of added acetophenone. For interlaboratory comparison and for comparison of analyses involving different columns, peak area measurements are recommended, even though the standard deviations are slightly higher than for peak height measurements.

The main peaks in the chromatograms have been identified, including that of the reaction product between TGDDM and DDS. This peak is useful for following the ageing of a prepreg.

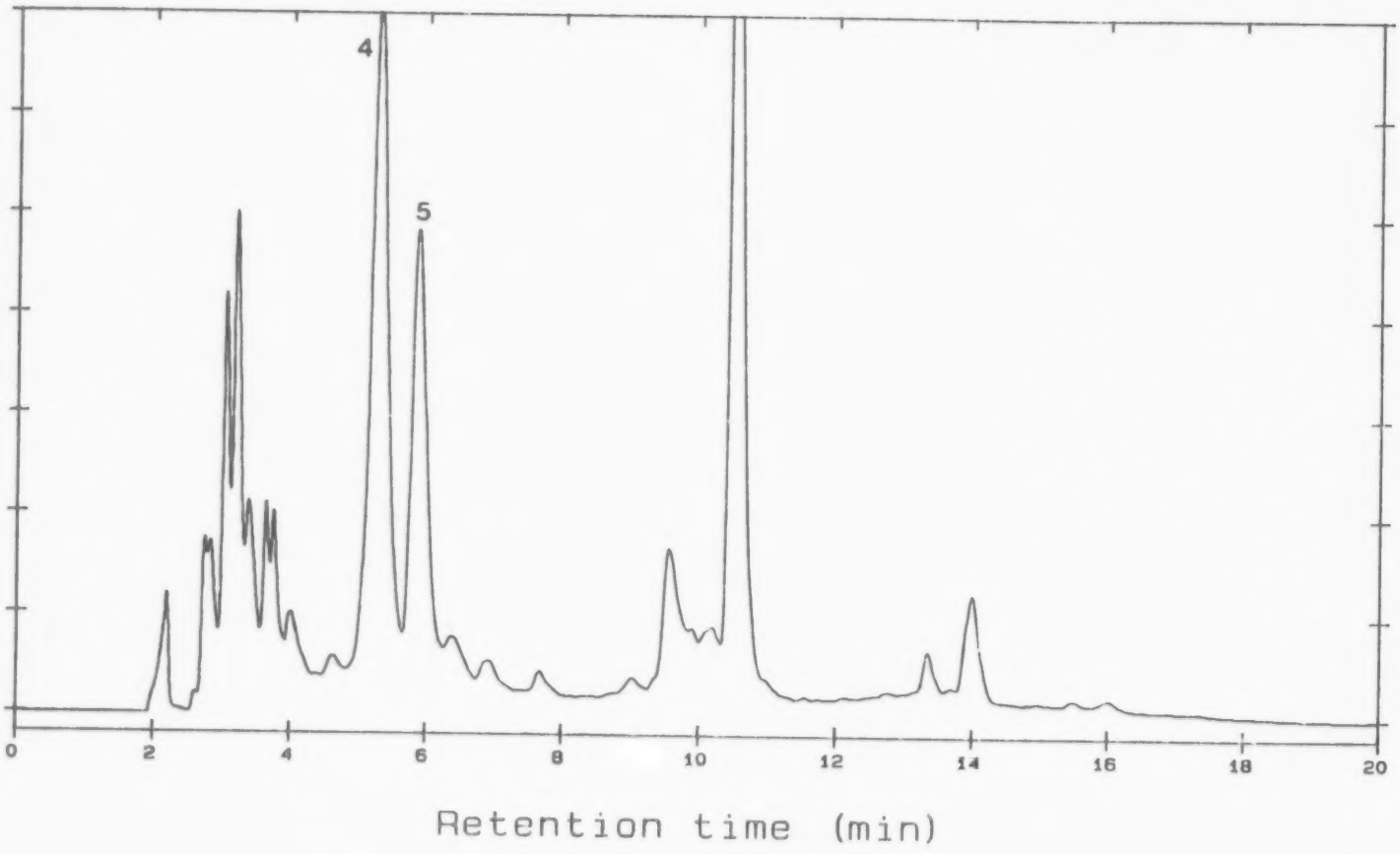


Figure 37: RPLC separation of a solution of Araldite MY 720 in a mixture THF/0.001 M HNO_3 after several days. Column: Hypersil ODS, 25 cm X 4.6 mm i.d..

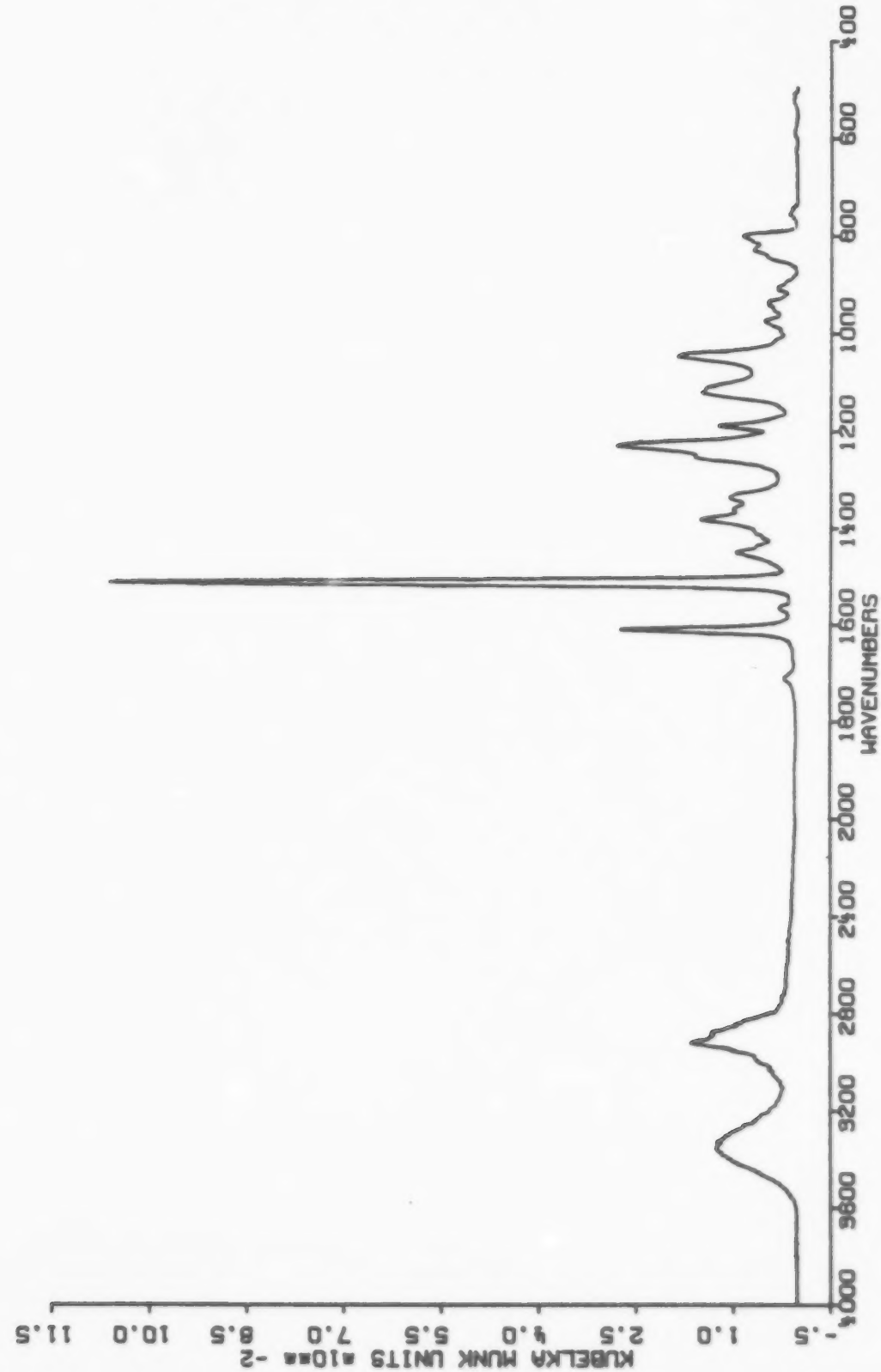


Figure 38: Infrared spectrum of peak #4 (Figure 37).

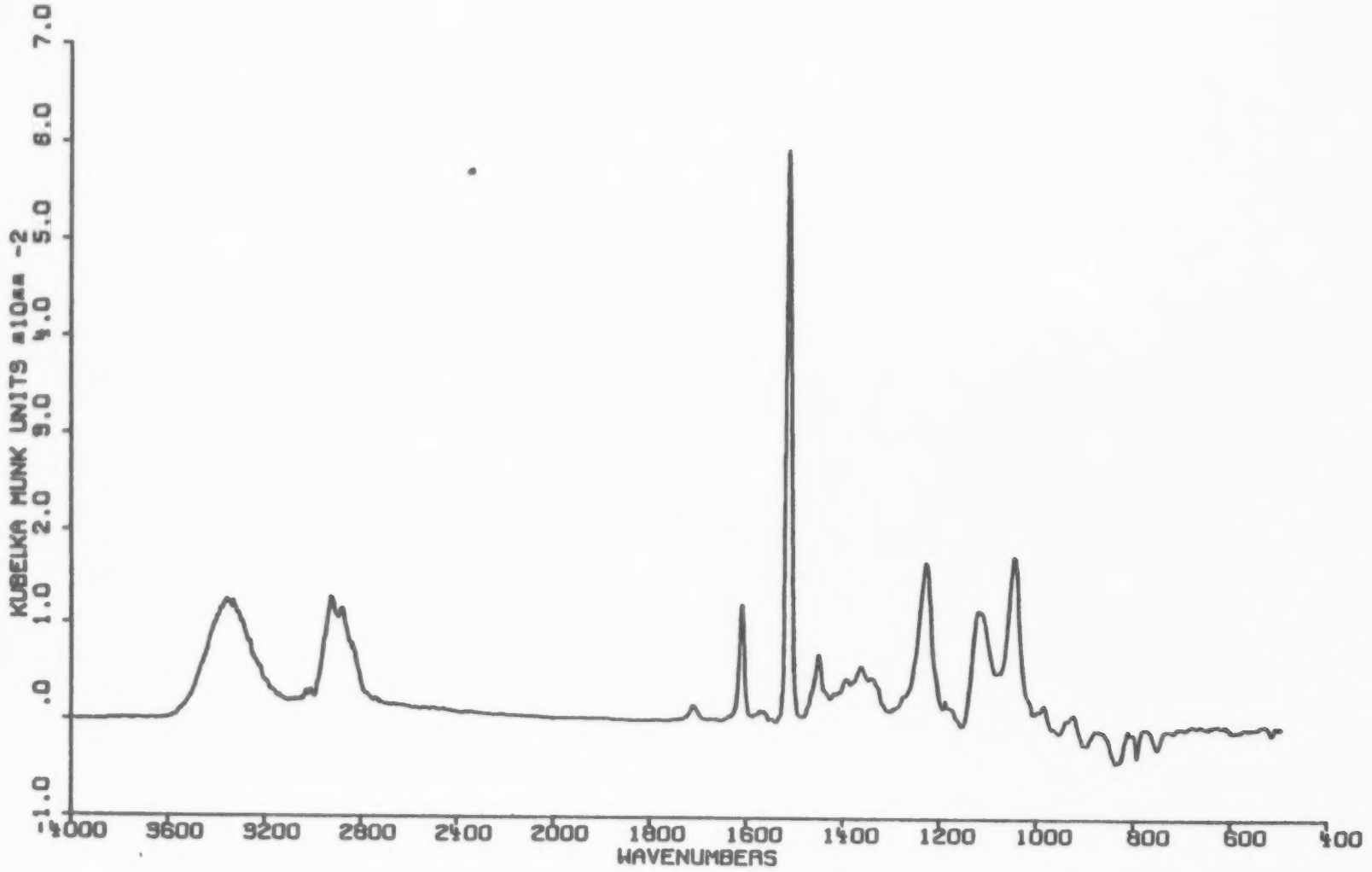


Figure 39: Subtraction: infrared spectrum of peak #4 minus infrared spectrum of the TGDDM peak (peak #9, Figure 2).

4. HIGH-SPEED REVERSE-PHASE LIQUID CHROMATOGRAPHY WITH 3 μm PACKING

4.1 Introduction

The previous section demonstrated the usefulness of reverse-phase liquid chromatography for analysing an epoxy resin system. However, the total analysis requires about 60 minutes because the column must be regenerated to its initial condition after the completion of the gradient run. With a column 30 cm long packed with 5 or 10 μm particles, this operation consumes considerable time and solvent. In addition to the regeneration requirement, the chromatographic separation must be optimized to obtain the best compromise between peak resolution and analysis time. The introduction of commercially available short reverse-phase columns packed with 3 μm particles has resolved this problem by substantially decreasing the separation time [16,17].

The purpose of this section is to demonstrate the usefulness of such columns for reducing the analysis time and the solvent consumption without a significant loss of resolution in the analysis of epoxy resins. As the instrumental parameters are more critical with a 3 μm packing [18], the basic parameters involved in separations using this type of column will be discussed.

4.2 Column efficiency

Various parameters have been defined in chromatography theory in order to evaluate the quality of a separation. Some of them will be briefly described as a basis for comparing the performance of different chromatographic stationary phases. The efficiency of a chromatographic column is expressed quantitatively as the number of theoretical plates per unit length or its inverse, the height equivalent to a theoretical plate (HETP):

$$H = L/N$$

where L is the column length and N is the total number of theoretical plates. The parameter H is preferable to the number of theoretical plates alone to describe adequately the efficiency of a chromatographic column [19]. In the calculation of H, N is obtained by measuring the retention time t_R and the half-height width W_h of a given peak:

$$N = 5.54 (t_R/W_h)^2$$

The degree of resolution of two peaks is influenced by the magnitude of the relative band spreading, which is related to the HETP. Thus, for a column of length L, a decrease in HETP corresponds to an increase in the number of theoretical plates N and hence an increase in the resolution. Consequently, it is very important to minimize the HETP value to obtain a good separation.

There are four sources of band spreading in liquid chromatography: (1) eddy diffusion; (2) longitudinal diffusion; (3) mass transfer; and (4) extra-column tubing. The overall HETP can be expressed as the sum of all these contributions.

Assuming that extra-column volumes are kept constant and as low as possible in a chromatographic system, the fourth parameter can be neglected. Mathematical expressions have been developed to relate the remaining three factors to experimental parameters such as solvent linear velocity and the particle size of the packing [20].

Figure 40 shows a plot of the height equivalent to a theoretical plate versus the flow rate as measured for anthracene in 60% acetonitrile - 40% water with three columns having different particle diameters. The variation of H is expressed as a function of the flow rate instead of the linear velocity to facilitate the comparison of different columns. With the 3 μm particles, the HETP remains almost constant as the flow rate increases whereas H increases rapidly with the flow rate for the 5 and 10 μm packings. Eddy diffusion, which corresponds to flow paths of different lengths in the column, is not highly dependent on the linear velocity of the mobile phase. This term can be minimized by decreasing the particle diameter and maintaining a uniform packing [20]. At high linear velocity, the longitudinal diffusion contribution, which is related to the dispersion of a sample under the influence of molecular diffusion, becomes negligible, since it is inversely proportional to the velocity.

The mass transfer term is the most important in liquid chromatography. Mass transfer describes the time taken by a solute to leave the particle by diffusion. The mass transfer contribution is proportional to the product d_p^2u, where u is the mobile phase linear velocity and d_p is the particle size of the stationary phase. Consequently, a decrease of the particle diameter of the stationary phase allows the use of a higher linear velocity (or flow rate) without increasing the height equivalent to a theoretical plate. As shown in Figure 40, the range of optimum flow rates is about 0.8-1.0 mL/min with the 10 μm packing whereas it is about 1.5-4.5 mL/min with the 3 μm stationary phase. Consequently, a column packed with 3 μm particles can be used at a higher flow rate without a significant loss of efficiency.

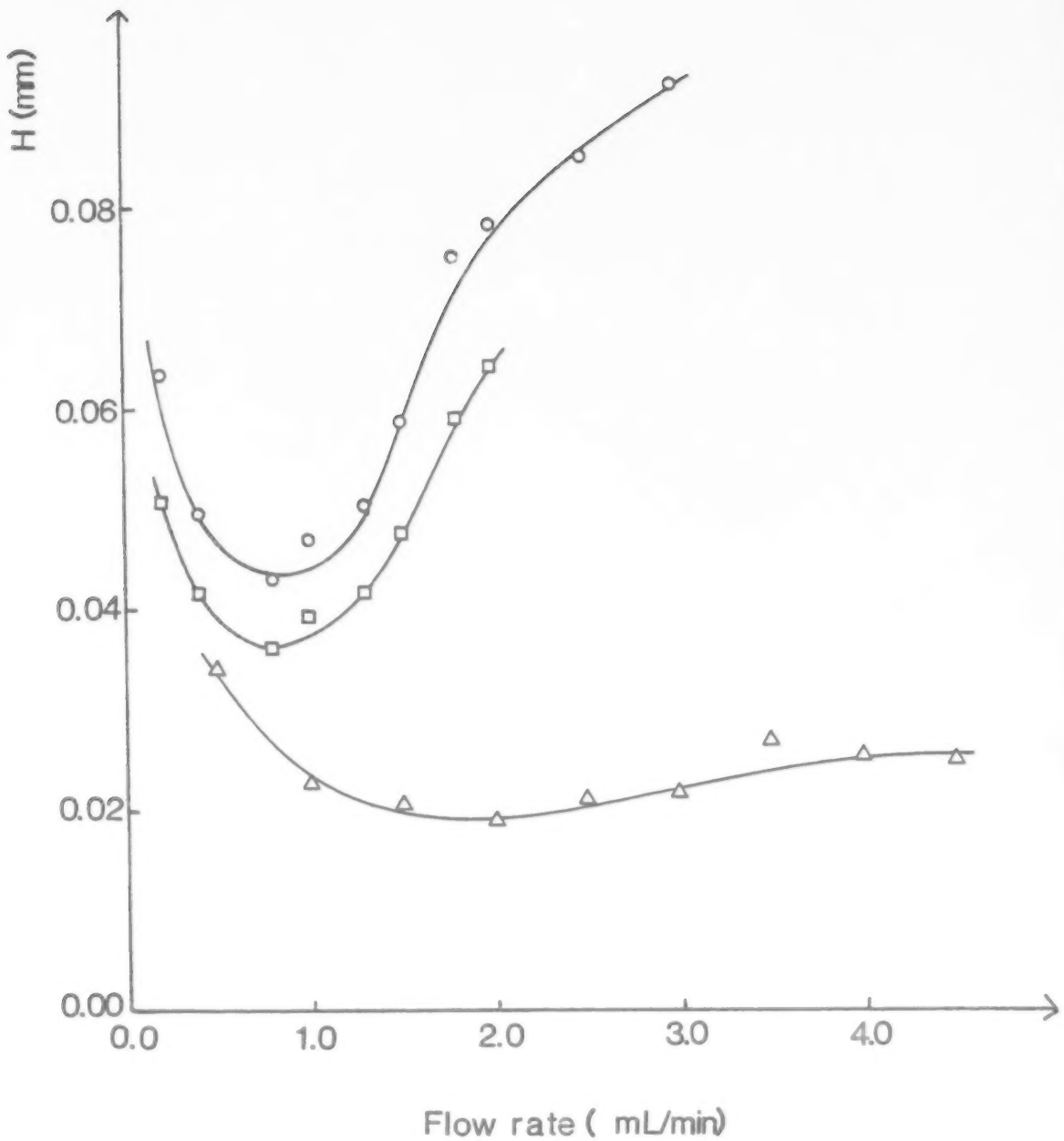


Figure 40: Variation of the height equivalent to a theoretical plate as a function of the flow rate for anthracene in 60% acetonitrile - 40% water with three columns having different particle diameters: (o) MCH-10-n-CAP, 30 cm X 4.0 mm i.d., 10 µm; (□) 5-n-CAP, 30 cm X 4.0 mm i.d., 5 µm; (△) Ultra-fast C_{18}-3, 4.0 X 4.6 mm c.d., 3 µm.

The possibility of using higher flow rates means that the analysis is completed in less time and that the solvent consumption is decreased substantially. This can amount to significant savings on a long-term basis for a quality control laboratory as shown in the next section.

4.3 Separation of Narmco 5208 resin

4.3.1 Optimization of the method

Figure 41 shows the separation of a THF extract of Narmco Rigidite 5208/WC3000 prepreg on an MCH-5-n-CAP column and on an Ultra-fast C_{18}-3 column. Both stationary phases are octadecyl bonded phases. For the short column, the initial eluent 20%/80% ACN/H_2O was increased linearly to 100% ACN over 3 minutes at a flow rate of 2.0 mL/min, kept at this composition for two additional minutes, and returned to the initial state within 0.1 minutes. For the longer column, details are given in Section 3.3. In both cases, the detection wavelength was 230 nm and the column temperature was kept at 25°C.

Several experiments were done with the two columns in order to obtain the maximum resolution in the shortest time. It was found that the separation is better on the 4 cm column packed with 3 µm particles if the starting eluent contains a larger proportion of water in comparison to the 30 cm long column. This is probably caused by the need to reduce the mass transfer efficiency with the 3 µm particles by using a weaker eluent.

With the 3 µm packing, the separation time is reduced from 25 minutes to 6 minutes. The resolution is almost as good as with the 30 cm long column. Peak #1, which is well separated from other major peaks, corresponds to the amine hardener (DDS). Peak #4 corresponds to TGDDM monomer from the major epoxy resin and peak #5 to DGEBA from the minor epoxy (Novolac). Peak #3 is the initial reaction product of TGDDM and DDS. Finally, peak #2 corresponds to acetophenone, which can be added as an internal standard to serve as a reference for quantifying the various peaks of the chromatogram, as described in the previous chapter.

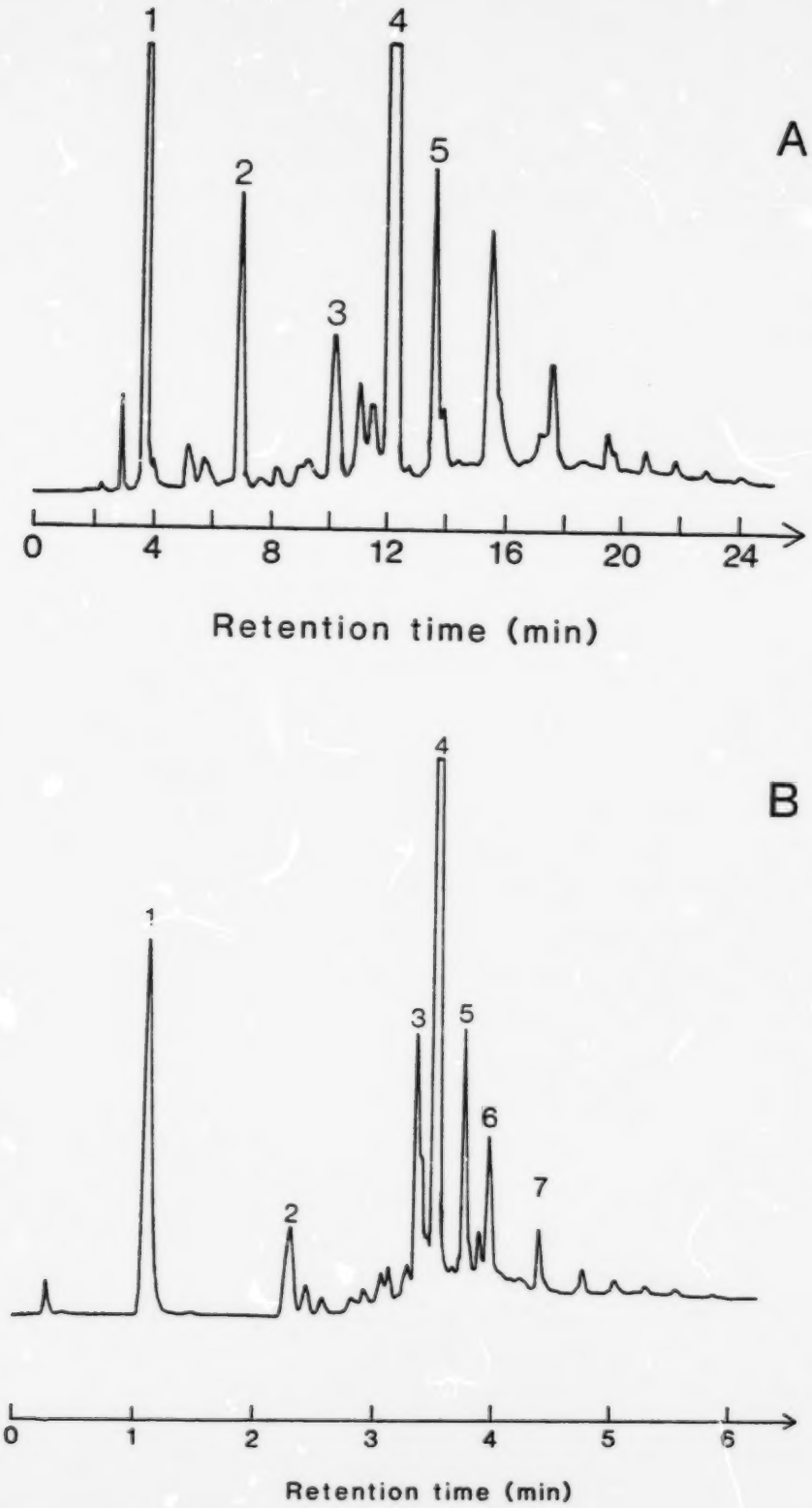


Figure 41: Separation of the extract of Narmco 5208 prepreg:
(A) MCH-5-n-CAP column, 30 cm X 4.0 mm i.d., 5 µm particles;
(B) Ultra-fast C_{18}-3, 4.0 cm X 4.6 mm i.d., 3 µm particles.

4.3.2 Column regeneration

The column regeneration time is also considerably reduced with the 4 cm long column. Figure 42 shows the effect of the regeneration time on the measured retention time of the TGDDM peak for both columns. With the 5 µm packing, a regeneration time of about 30 minutes is necessary to obtain a reproducible retention time, whereas with the 3 µm packing, a regeneration time of 4 minutes is sufficient. Thus, the overall analysis on the 4 cm column is accomplished in 10 minutes at a flow rate of 2 mL/min, compared to 60 minutes at 1 mL/min on the ordinary column. Consequently, the use of the high-speed column reduces solvent consumption by a factor of three and overall analysis time by a factor of six.

The same advantages apply to quality control testing of other raw materials. For example, impurities in the hardener DDS can be detected in less than three minutes (Figure 43).

4.3.3 Comparison of different batches of Narmco 5208 resin

The different batches of Narmco 5208 analysed by RPLC on ordinary columns as described in Section 3.6 were also analysed by HS-RPLC. They were as follows: five prepregs (batches #1101, #1103, #1104, #1010, #1014), the neat resin on a plastic backing sheet (batch #1047), and the neat resin in bulk form (batch #1023). Resins were dissolved in tetrahydrofuran and injected three times after filtration. Table 19 gives the results expressed in terms of normalized areas with respect to acetophenone internal standard, and as area ratios with respect to the TGDDM peak. The peak numbering is shown in Figure 41.

Direct comparison of these results with those of Table 15 (MCH-5-n-CAP column, 30 cm x 4.0 mm i.d., ordinary RPLC) is complicated for a number of reasons. Firstly, the results of Table 15 were obtained in January 1985, while those of Table 19 were obtained in July 1986, and some aging may have occurred in the interval. This is especially true for batch #1014, which was handled more frequently than the others. This would explain why the figures obtained for free DDS, TGDDM, and DGEBA are generally lower in Table 19 than in Table 15. It could also explain why the figures for the reaction product peak (RP) are higher, but there is a second explanation as well. With the high-speed column, this peak is less well resolved than with the ordinary column, so it includes contributions from other peaks. Thirdly, the different resolution with the high-speed column means that the

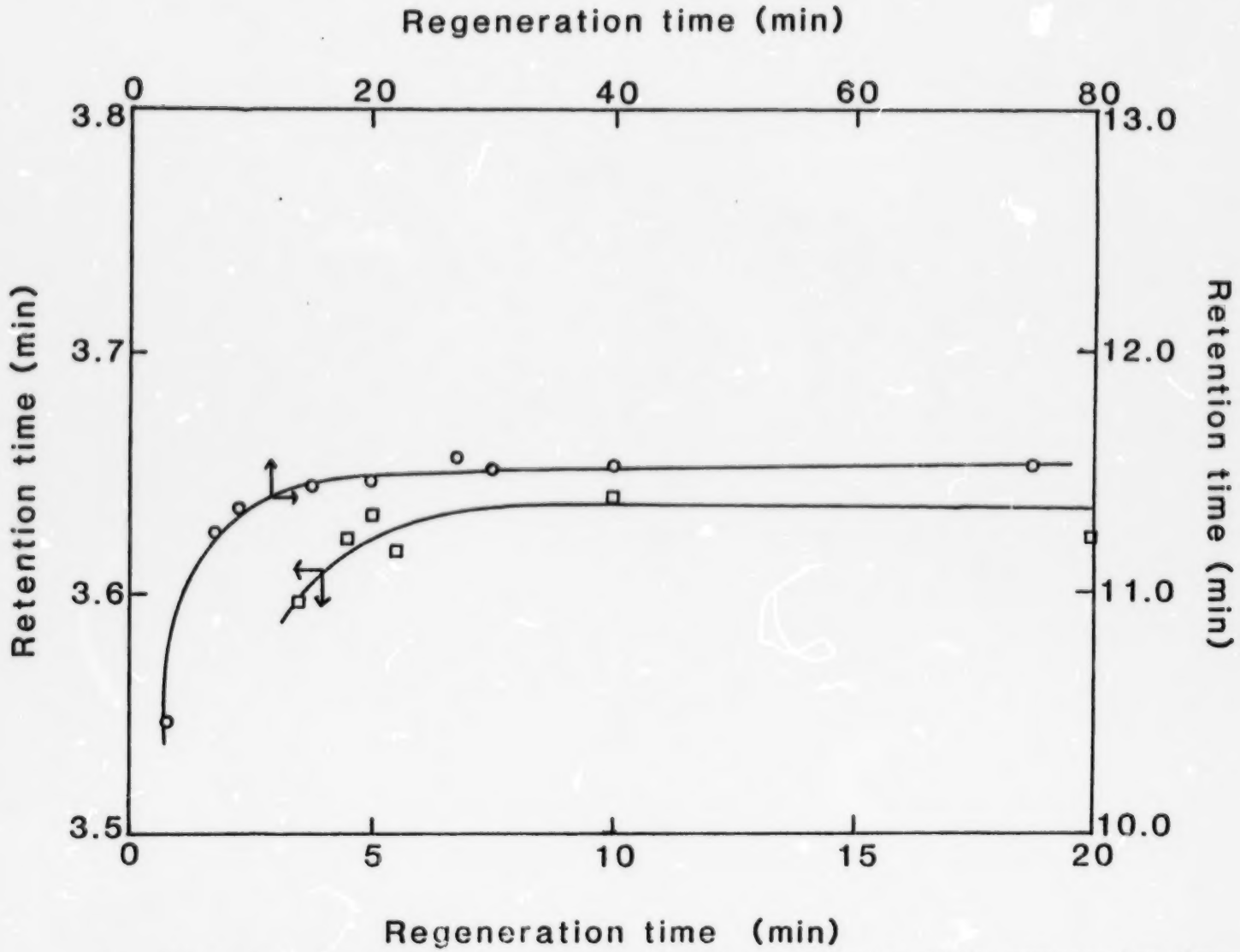


Figure 42: Retention time of the main peak (TGDDM) as a function of the regeneration time:
(O) MCH-5-n-CAP column, 30 cm X 4.0 mm i.d., 5 µm particles
(□) Ultra-fast C_{18}-3, 4 cm X 4.6 mm i.d., 3 µm particles.

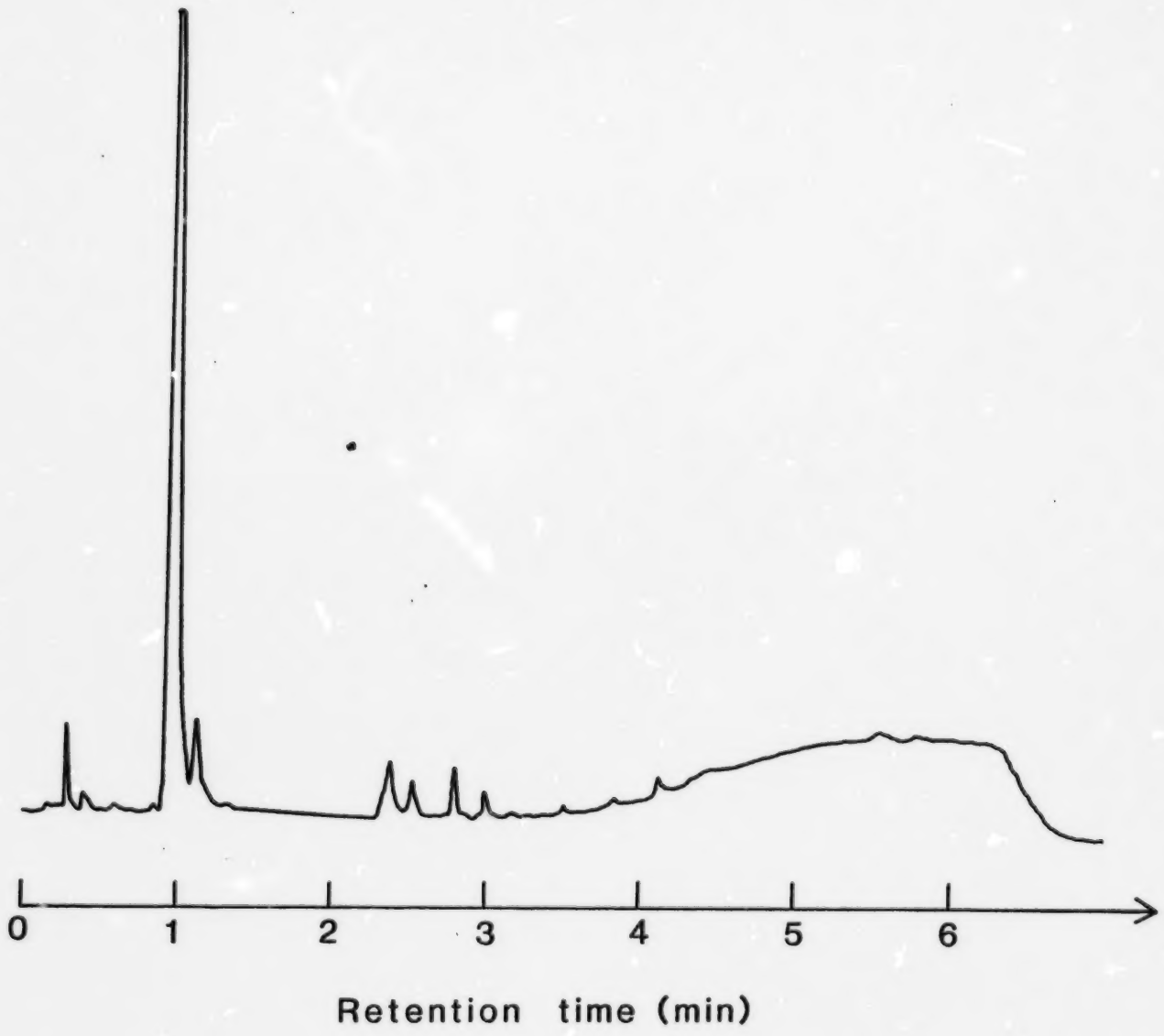


Figure 43: HS-RPLC separation of Hardener HT976
Column: Ultra-fast C_{18}-3, 4 cm X 4.6 mm i.d., 3 µm particles.

drawing of the baseline is somewhat different, and this can affect the calculated peak areas. In spite of these differences, the HS-RPLC results and the ordinary RPLC results lead to similar conclusions. Batch #1023 is the most advanced, while batch #1047 is the least advanced and contains an unusually low amount of Novolac.

Table 19. HS-RPLC results for different batches of the Narmco 5208 system; normalized areas with respect to acetophenone internal standard, and area ratios w. r. t. TGDDM

Peak	1103	1101	1104	1010	1014	1047	1023
1 (DDS)	3.292	3.555	3.212	3.241	2.604	4.481	2.737
3 (RP)	3.020	2.862	3.073	3.106	3.314	1.260	4.449
4 (TGDDM)	12.12	12.09	12.19	11.82	11.08	15.81	12.27
5 (DGEBA)	1.364	1.168	1.230	0.926	1.232	0.564	0.606
6	0.997	1.076	0.895	0.739	0.639	1.004	0.789
7	0.262	0.244	0.246	0.252	0.264	0.198	0.102
1/4	0.272	0.294	0.263	0.274	0.235	0.283	0.223
3/4	0.249	0.237	0.252	0.263	0.299	0.080	0.363
5/4	0.112	0.097	0.101	0.078	0.111	0.036	0.049

For quantitative analyses over a long time period, it is advisable to consistently use the same type of column, either a long column (25 cm) packed with 5 μm particles, or a short one (4 cm) packed with 3 μm particles. For some applications, the high resolution of a longer column is not needed and HS-RPLC will be more than adequate for controlling the quality of a product.

4.4 Instrumental considerations

In this work, short columns with 3 μm particles were used without modification of the chromatographic system. It is well known that extra-column volumes (e.g. capillary tubing connections, flow cell, etc.) must be minimized to reduce the extra-volume dilution. The standard cell with the UV-100 detector has a volume of 4.5 μL and it was not found necessary to change the flow cell for a smaller one to obtain an acceptable bandwidth. Of course, a decrease in the volume of the flow cell would improve the number of theoretical plates but if the instrument is used with conventional columns also, it is more convenient to use a medium-size detector flow cell. If a small-volume injector is available, it is

recommended not to inject a sample volume greater than 6 µL to avoid damaging the column. The 3 µm packing is more fragile than 5 µm particles but the improvement in the analysis time is considerable. As stipulated elsewhere [17], it is recommended to carefully clarify the sample and the mobile phase before the injection.

4.5 Conclusion

Short columns packed with 3 µm packing are useful when the separation does not need a high number of theoretical plates and when the rapidity of analysis is important. It has been shown that these high-speed columns can be used advantageously to analyse the composition of an epoxy-graphite prepreg. The results obtained with the high-speed columns correlate well with those found using other analytical techniques.

5. HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY

5.1 Introduction

Size-exclusion chromatography (SEC) is a liquid chromatographic technique which separates molecules according to their size. It is sometimes referred to as "gel permeation chromatography". Yau et al. [21] have defined high-performance size-exclusion chromatography (HPSEC) as "a system in which the number of theoretical plates generated per second is about tenfold greater than that of traditional SEC systems. This means that separations commonly will take 10-20 minutes compared to the much longer (hours) separations of conventional size-exclusion chromatography." This improvement was made possible through the use of highly crosslinked poly(styrene/divinylbenzene) macroporous particles. With 5 μm particles, an epoxy resin separation can be done with a single column rather than the four or five columns usually required in SEC.

The resolution on a SEC column is not as good as that obtained in HPLC. However, information on the molecular weight distribution can be useful and the SEC method can be an alternative to the HPLC method for quality control of a prepreg.

5.2 Separation of Narmco 5208 resin

In SEC, the optimization of a separation is relatively easy to achieve in comparison to HPLC because the mobile phase is usually composed of a single component, typically tetrahydrofuran or chloroform. The HPSEC column used in this work was a PLgel column, 30 cm long x 7.5 mm i.d., packed with 5 μm particles of a poly(styrene/divinylbenzene) copolymer. The mobile phase was tetrahydrofuran with a flow rate of 1.0 mL/min, and UV detection at 254 nm was used.

Figure 44 shows a chromatogram of the extract of Narmco 5208 epoxy prepreg, batch #1103, on the PLgel column. The separation is achieved in less than 7.5 minutes with good resolution. In comparison, the same separation with a similar resolution required 40 minutes with five Styragel columns [22].

Figures 45 to 47 represent respectively the chromatograms of epoxy resins Araldite MY 720 and Epi-Rez SU-8 and of Hardener HT 976. Comparison with Figure 44 shows that the peak at 6.8 minutes corresponds mainly to DDS and the peak at 7.1 minutes to TGDDM. The molecular weight of DDS is 248.3 g/mol whereas that of TGDDM is 422.5

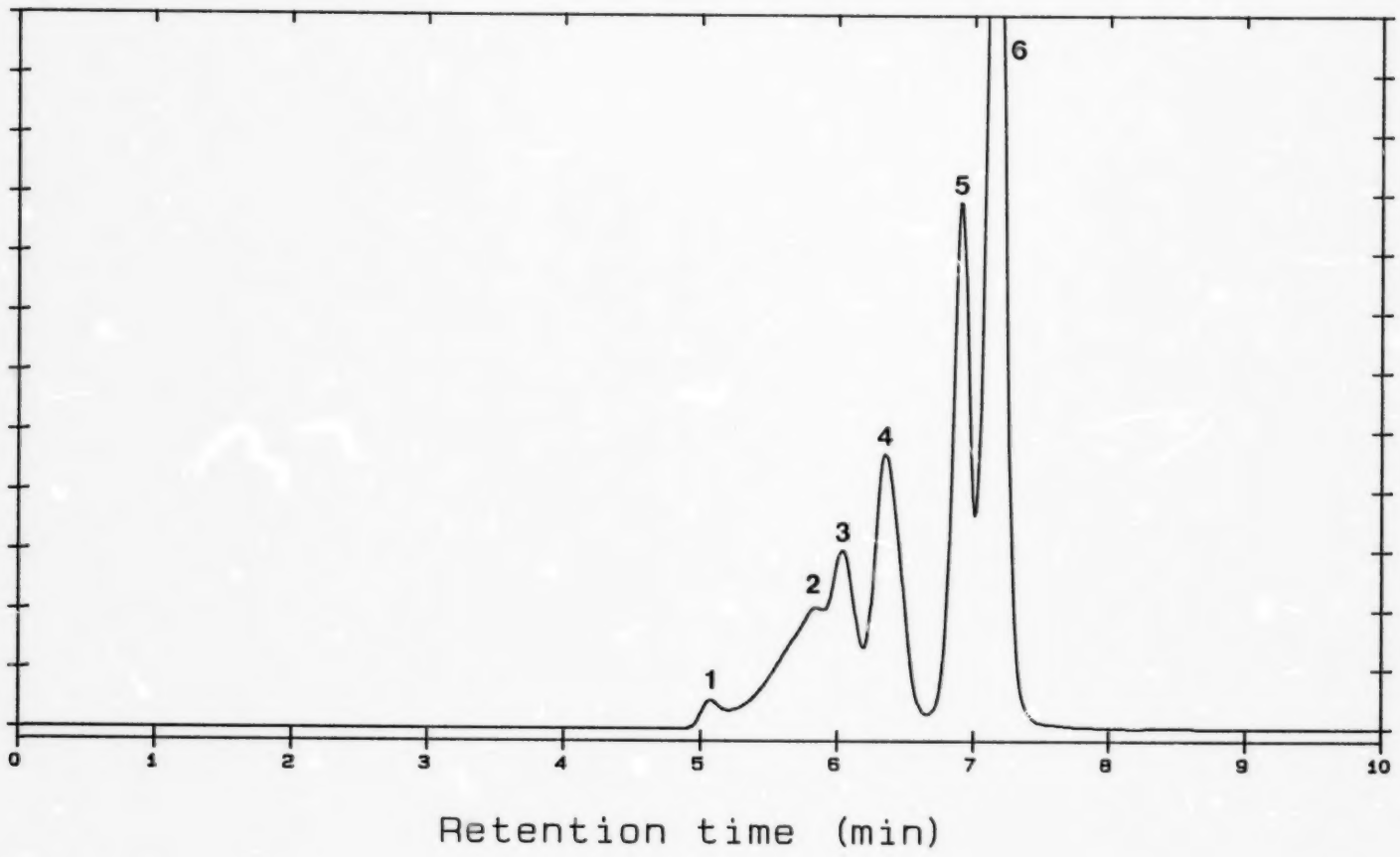


Figure 44: HPSEC separation of the extract of Narmco 5208 prepreg, batch #1103. Column: PLgel, 30 cm X 7.5 mm i.d..

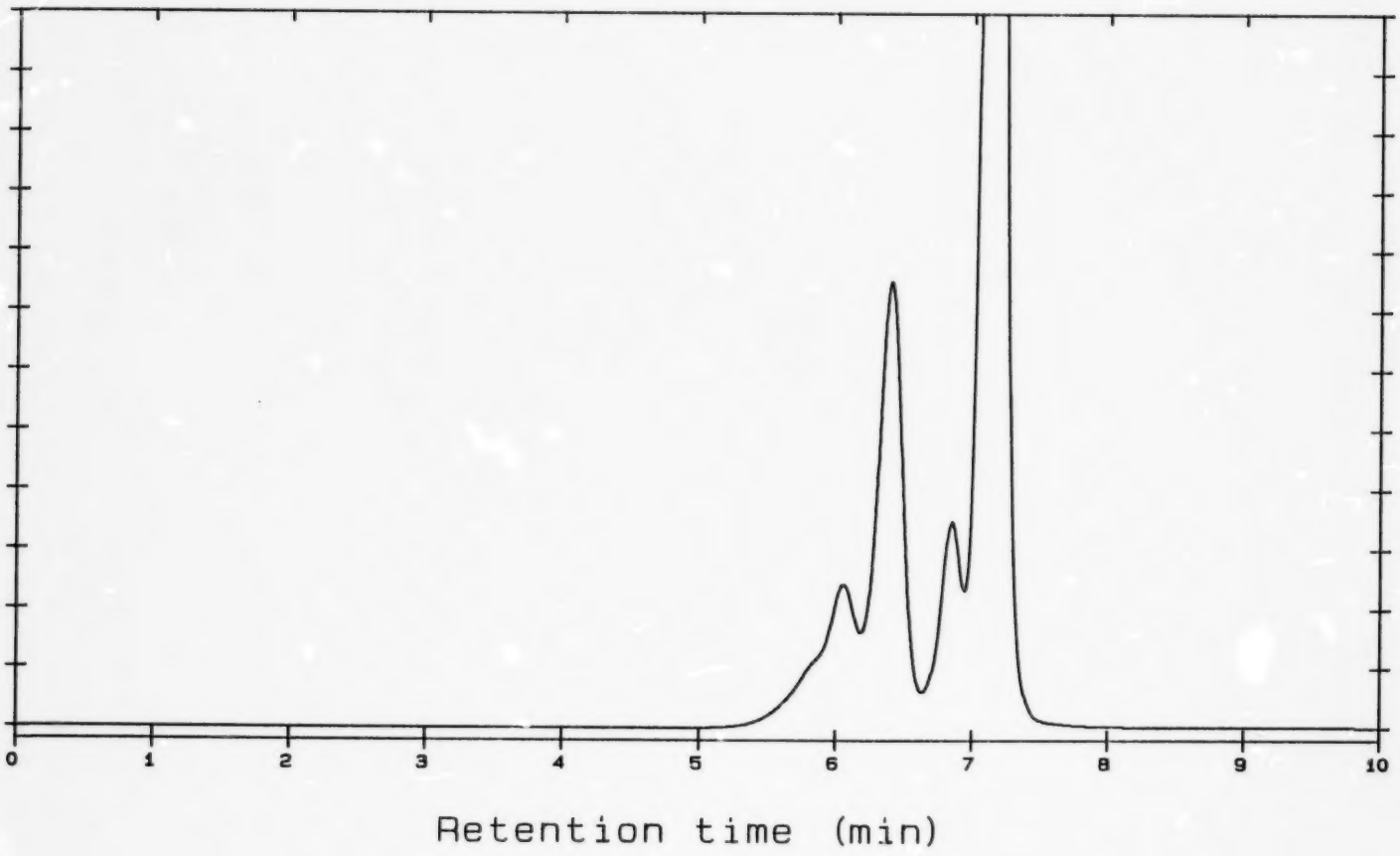


Figure 45: HPSEC separation of a solution of Araldite MY 720 in THF.
Column: PLgel, 30 cm X 7.5 mm i.d..

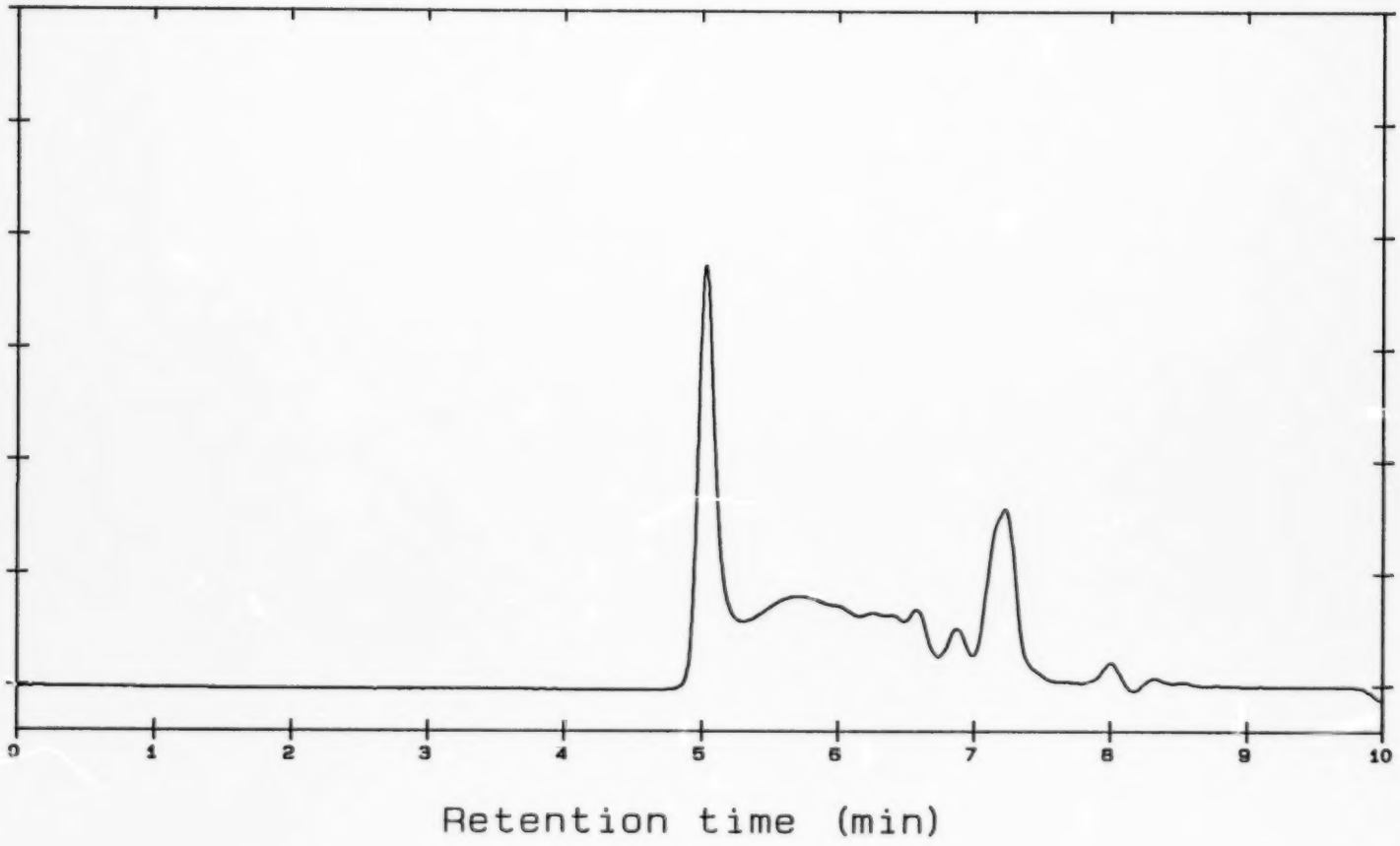


Figure 46: HPSEC separation of a solution of Epi-Rez SU-8 in THF
Column: PLgel, 30 cm X 7.5 mm i.d..

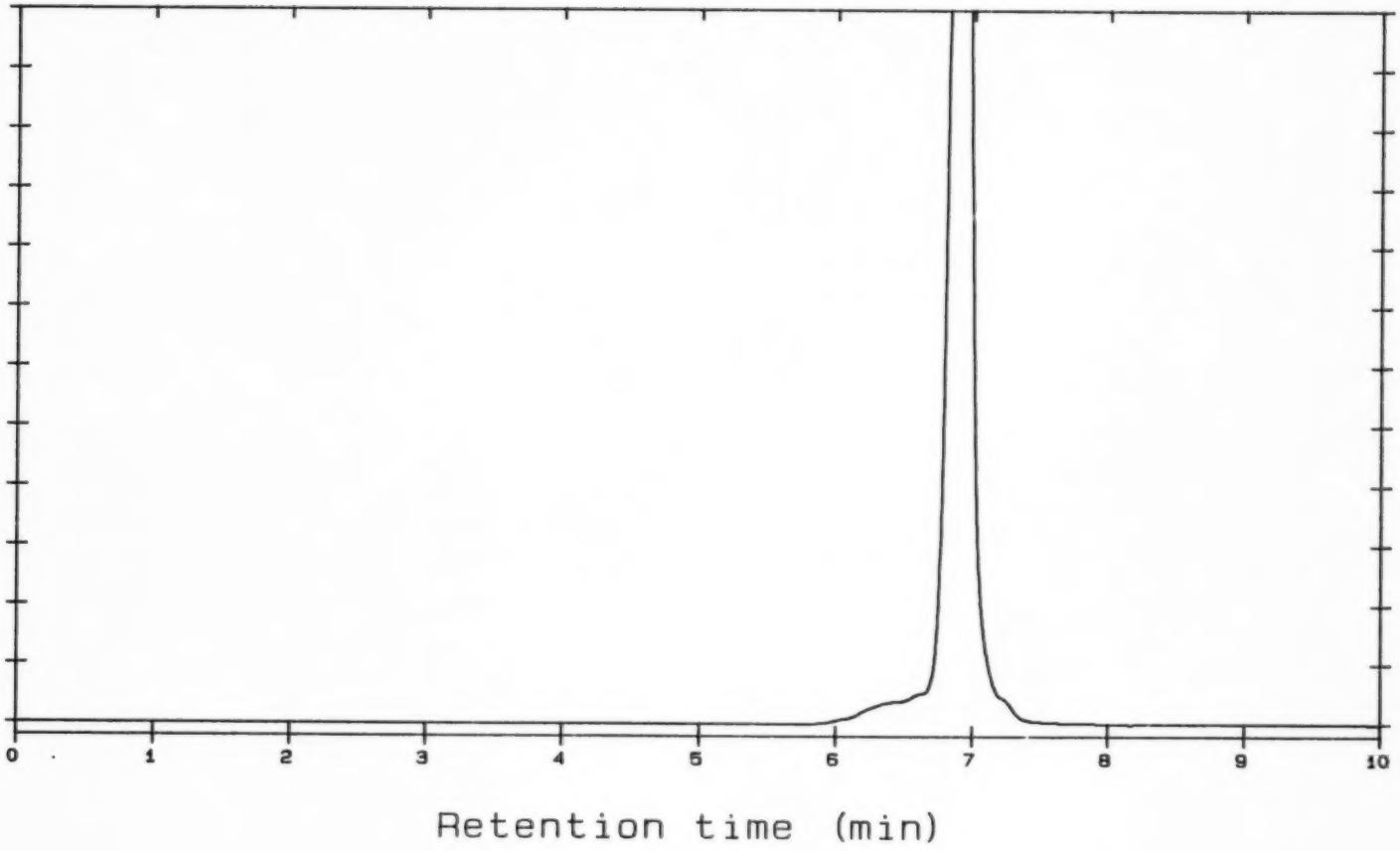


Figure 47: HPSEC separation of a solution of Hardener HT 976 in THF
Column: PLgel, 30 cm X 7.5 mm i.d..

g/mol. However, DDS is eluted before TGDDM, which is contrary to the behavior expected in size-exclusion chromatography. This is explained by the ability of THF to form strong hydrogen bonds with the amino groups of the DDS, thus increasing the effective size of the molecule. To verify this hypothesis, separate solutions of MY 720 and HT 976 were injected on the same column but with chloroform as eluent. In this case, as shown in Figure 48, DDS is eluted at 6.9 minutes whereas TGDDM is eluted at 6.6 minutes. (The peak at 8.1 min arises from the THF.) Thus, DDS is eluted after TGDDM because $CHCl_3$ cannot form hydrogen bonds. Evidence for hydrogen bonding between DDS and THF has also been observed in infrared spectroscopy (Part 2, Section 3.2). However, with $CHCl_3$ the resolution between DDS and TGDDM is almost nonexistent, so $CHCl_3$ should not be used with the PLgel column for the separation of this epoxy system.

5.3 Comparison of different batches of Narmco 5208 resin

Different batches of Narmco 5208 were analysed by HPSEC. They consisted of five prepregs (batches #1101, #1103, #1104, #1010, #1014), the neat resin on plastic backing sheet (batch #1047), and the neat resin in bulk form (batch #1023). Resins were dissolved in tetrahydrofuran and injected after filtration. Each solution was injected three times and the average of these values are reported. The chromatograms of batches #1103, #1023 and #1047 are given in Figures 44, 49 and 50. The others are similar to that of batch #1103.

The relative peak areas were measured for each batch and are reported in Table 20. Unlike the case of RPLC, the relative area in HPSEC can be evaluated with high precision because the baseline is quite stable. Also, as there are only 5 or 6 peaks, the computation of data is simpler and more reproducible. The relative standard deviation is always lower than 1% and often lower than 0.5%. The addition of an internal standard is less important because each peak generally corresponds to several compounds and thus, a variation of the peak area may reflect a variation in composition involving more than one compound. By comparing Figures 44 (#1103) and 49 (#1023), it can be seen that the amount of DDS (peak #5, 6.9 minutes) is lower for batch #1023. The low level of the minor epoxy resin (Novolac) in batch #1047 is evident on comparing Figures 44 and 50; the area of the peak #1 (near 5 minutes) is very small.

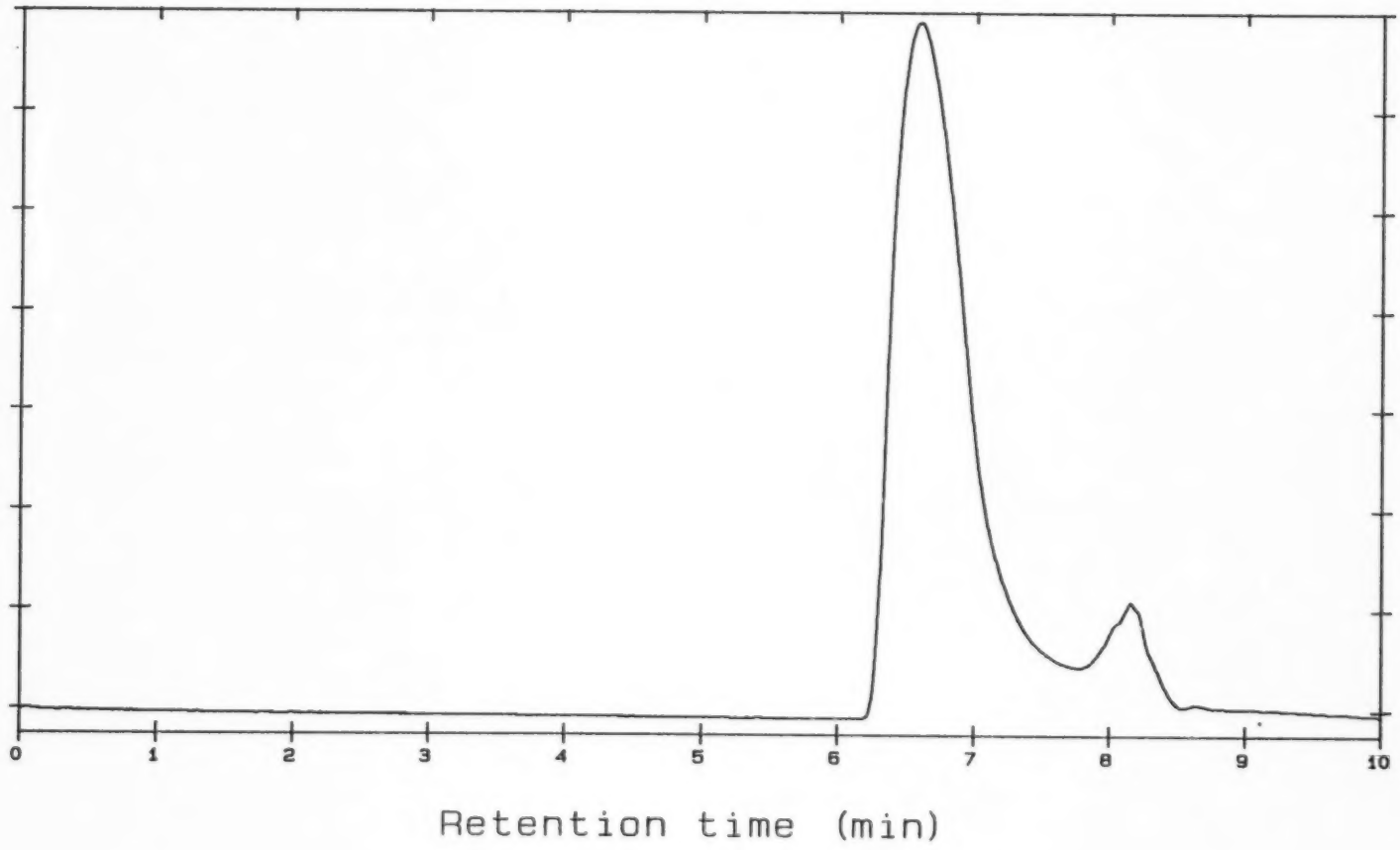


Figure 48(a): HPSEC separation of a solution of Araldite MY 720 in $CHCl_3$ as eluent.
Column: PLgel, 30 cm X 7.5 mm i.d..

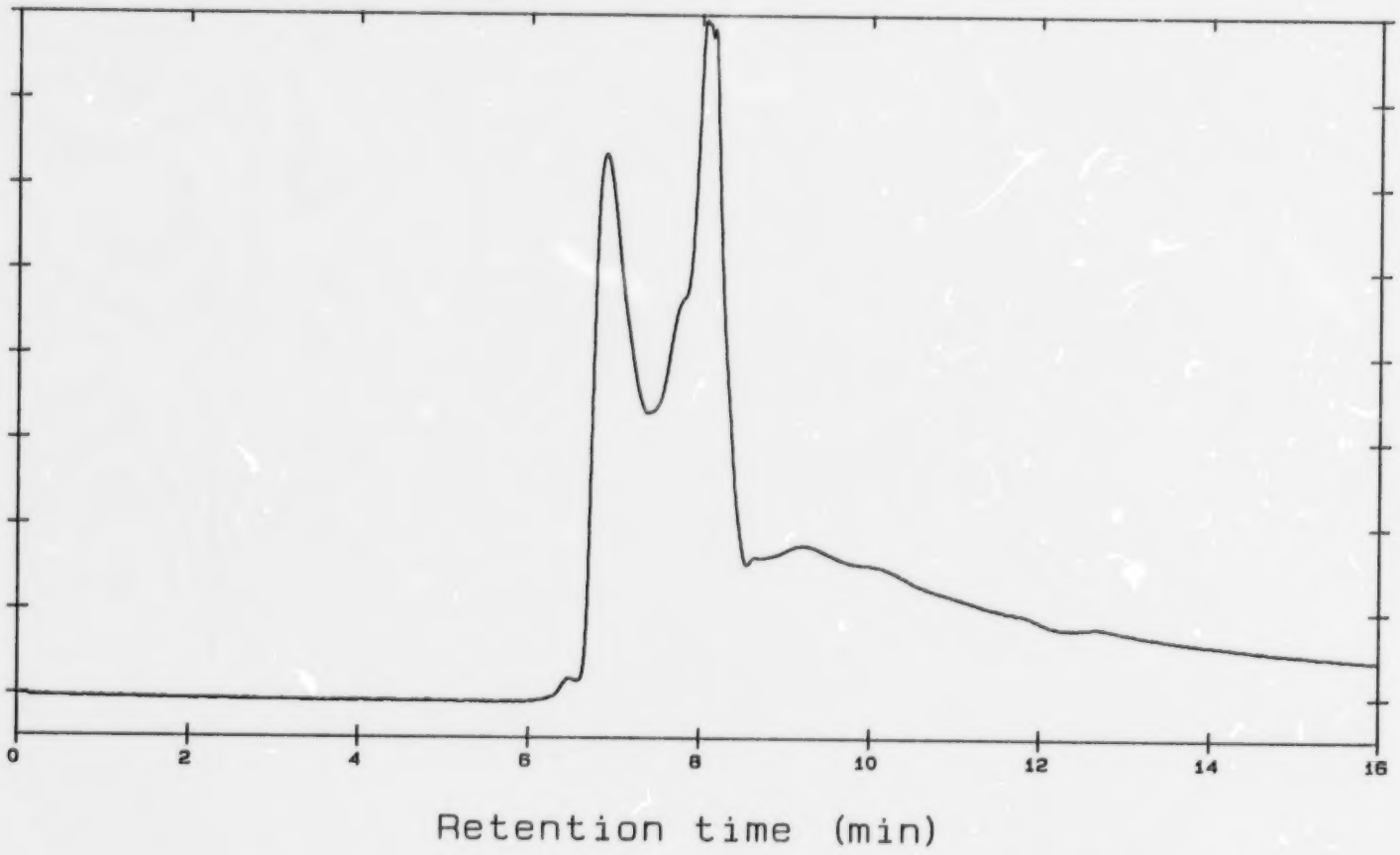


Figure 48(b): HPSEC separation of a solution of Hardener HT 976 in $CHCl_3$ as eluent. Column: PLgel, 30 cm X 7.5 mm i.d..

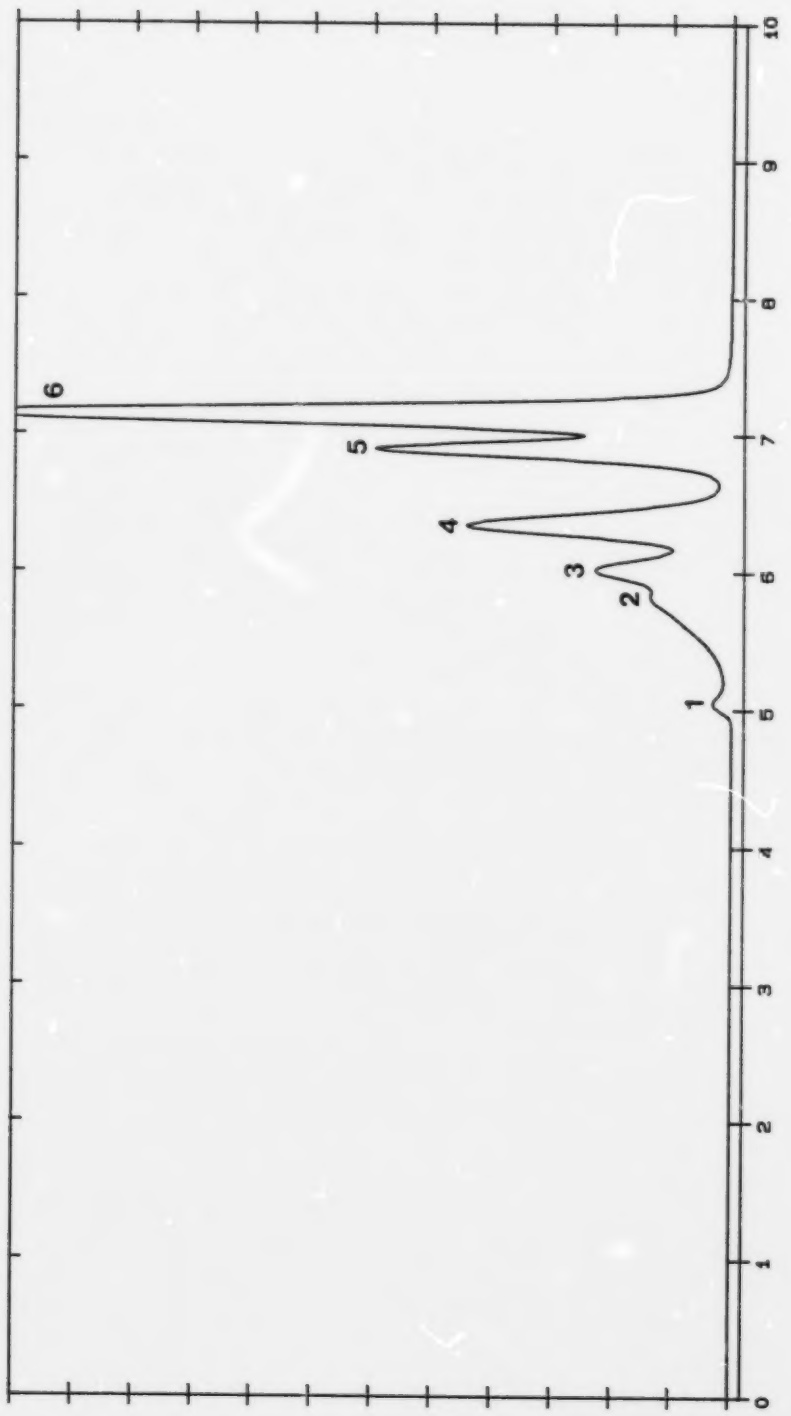


Figure 49: HPSEC of a solution of Narmco 5208 neat resin, batch #1023.
Column: PLgel, 30 cm X 7.5 mm i.d..

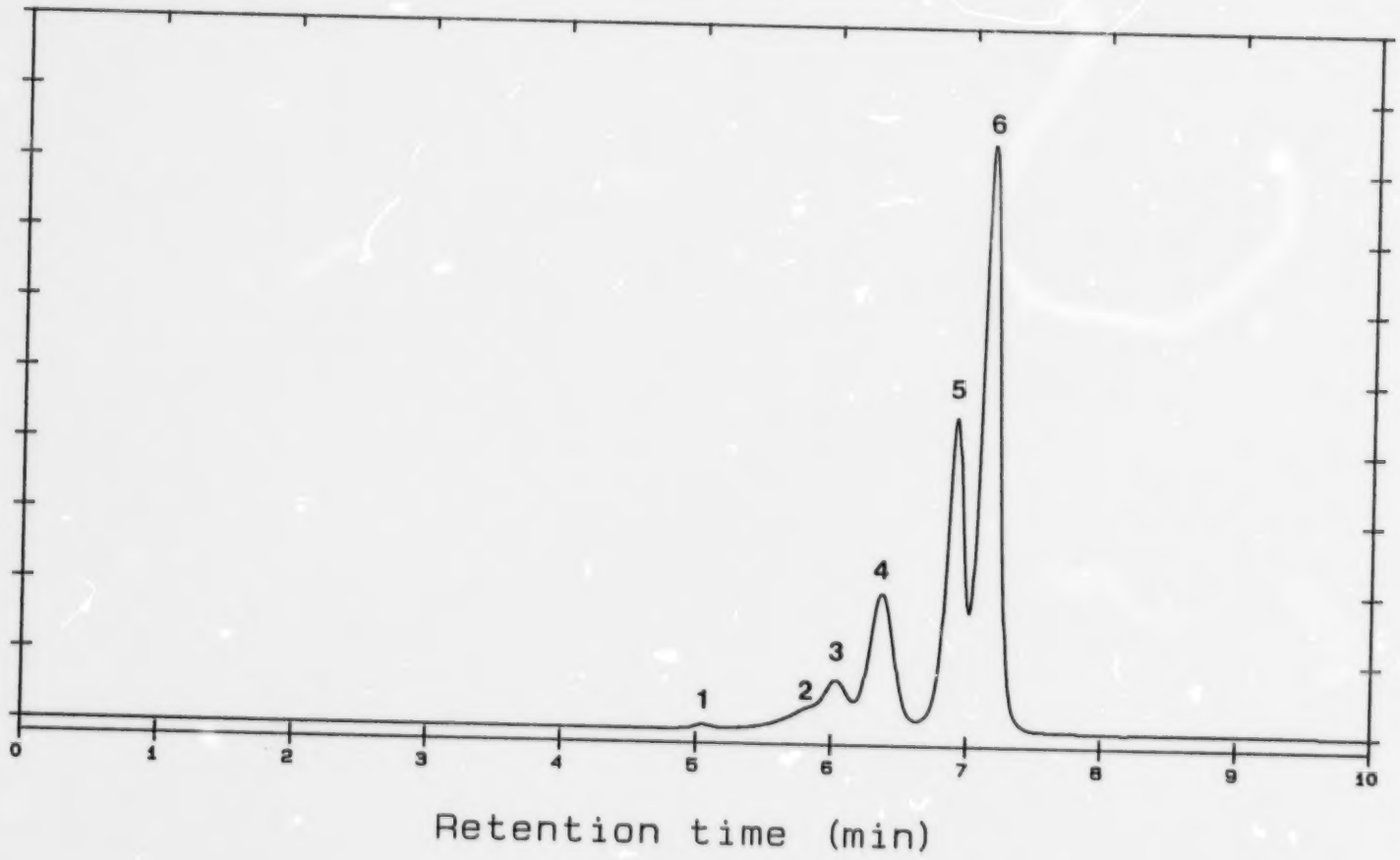


Figure 50: HPSEC separation of the extract of Narmco 5208 prepreg, batch #1047. Column: PLgel, 30 cm X 7.5 mm i.d..

Table 20. Relative peak areas for HPSEC analysis of different batches of the Narmco 5208 epoxy resin system.

Peak	1103	1101	1104	1010	1014	1047	1023
1 (Novolac)	1.38	0.96	1.13	0.78	1.16	0.39	1.09
2+3	22.07	17.92	19.70	15.20	20.38	8.88	18.84
4	16.73	16.23	16.31	19.26	18.73	16.07	18.69
5 (DDS)	20.74	22.80	21.37	23.87	20.60	25.30	18.49
6 (TGDDM)	38.98	42.04	41.46	40.82	39.06	49.15	42.76
(1 to 4) ÷ (5+6)	0.673	0.541	0.591	0.545	0.675	0.340	0.631

The last row of the table shows the figures obtained by dividing the total area of the first four peaks, corresponding to molecules of higher molecular weight, by the sum of the areas of peaks #5 and #6, which correspond mainly to monomers. These ratios are an indicator of the degree of polymerization, which would therefore appear to vary in the order: 1014 ≈ 1103 > 1023 > 1104 > 1101 ≈ 1010 > 1047. Comparison of the HPSEC data with the RPLC results (Tables 15 and 16) shows that the order of composition is not the same for the two methods. This is due to the fact that the HPSEC peaks correspond to the superposition of many molecules at the same retention time, whereas the RPLC peaks correspond to individual molecules such as the TGDDM-DDS reaction product. This makes the HPSEC results more difficult to interpret and generally means that HPSEC is less sensitive to variations in composition than is RPLC. Nevertheless, the HPSEC results corroborate the RPLC results to a certain extent. For example, both show that batches #1010 and #1101 are very similar, as are batches #1014 and #1103.

5.4 Effect of heating on the prepreg

The effect of heating on Narmco 5208 prepreg batch #1014 has been evaluated by RPLC (Section 3.8). The same solutions were injected on the HPSEC column to determine whether this technique could detect the variation. For this work, a refractive index detector was used, so the results cannot be directly compared with those of the previous section.

Figure 51 shows the chromatogram of the resin extracted from unheated prepreg. Figure 52 corresponds to the same prepreg after heating for 4 hours at 100°C. The peaks corresponding to DDS and TGDDM (7.0 and 7.3 min) have decreased in relative intensity and peaks corresponding to products of higher molecular weight (5 to 6.5 min) show a substantial increase, as a result of polymerization of the epoxy resin. The relative areas for both chromatograms are shown in Table 21. These data confirm the increase of high-molecular-weight compounds upon heating of the prepreg. Also, the ratio defined in the previous section changes significantly and can be a good indicator of the degree of advancement of the reaction. Because it depends on molecular size, SEC is particularly suited for monitoring the changes in molecular weight associated with the advancement of the resin.

Table 21. Effect of heating at 100°C on Narmco 5208 prepreg, batch #1014, PLgel column.

Peak	0 h	4 h
1 (Novolac)	7.54	5.43
2+3	14.38	32.08
4	20.51	17.73
5 (DDS)	19.77	13.31
6 (TGDDM)	37.80	31.45
(1 to 4) ÷ (5+6)	0.737	1.234

5.5 Conclusion

High-performance size-exclusion chromatography with a PLgel column allows rapid analysis of Narmco 5208 resin in less than 8 minutes. This technique is not as sensitive as RPLC for detecting variations among different batches, but can be useful for following variations in a given batch, such as changes in the degree of advancement.

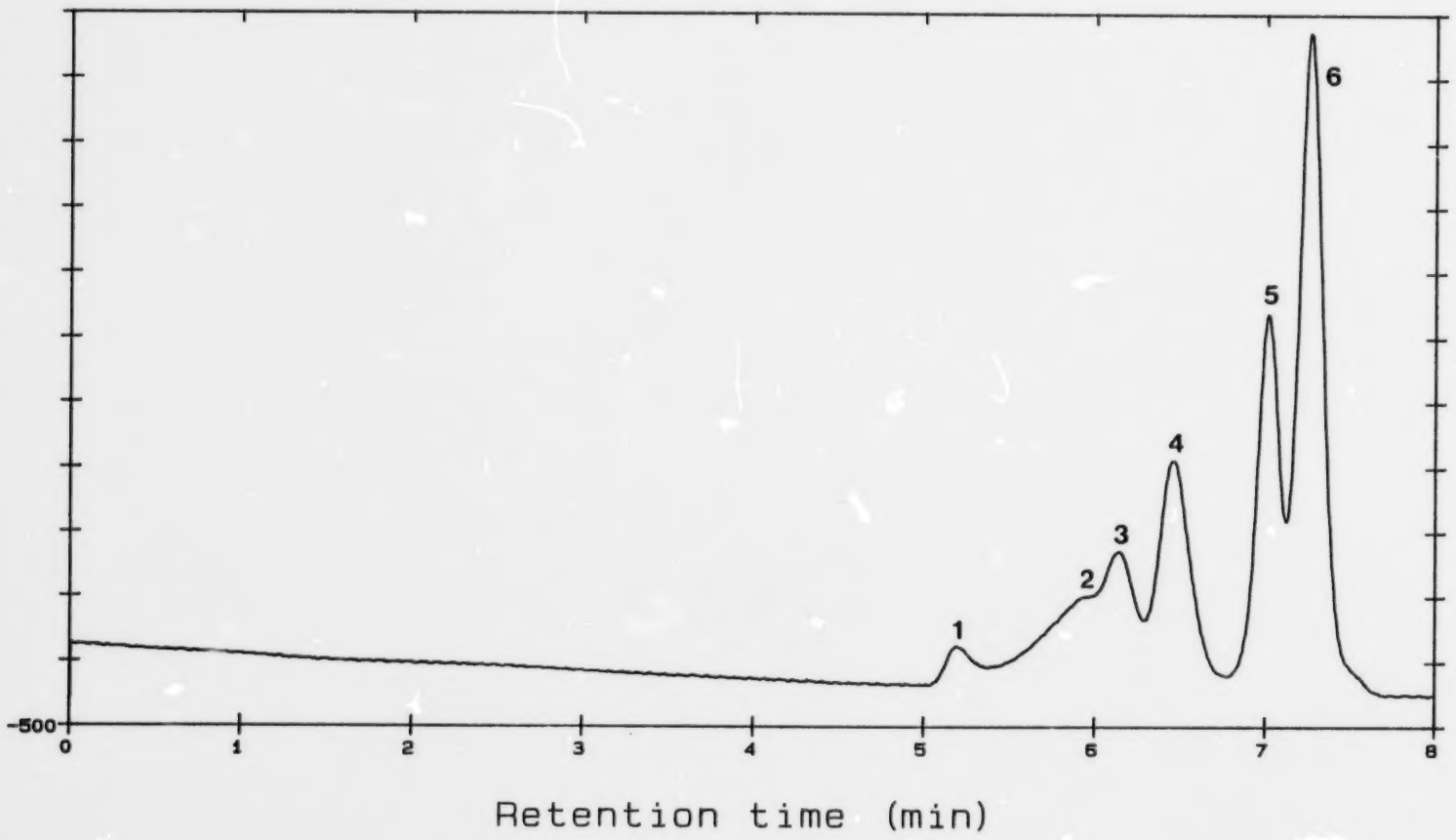


Figure 51: HPSEC separation of the extract of Narmco 5208 prepreg, batch #1014, unheated. Column: PLgel, 30 cm X 7.5 mm i.d..

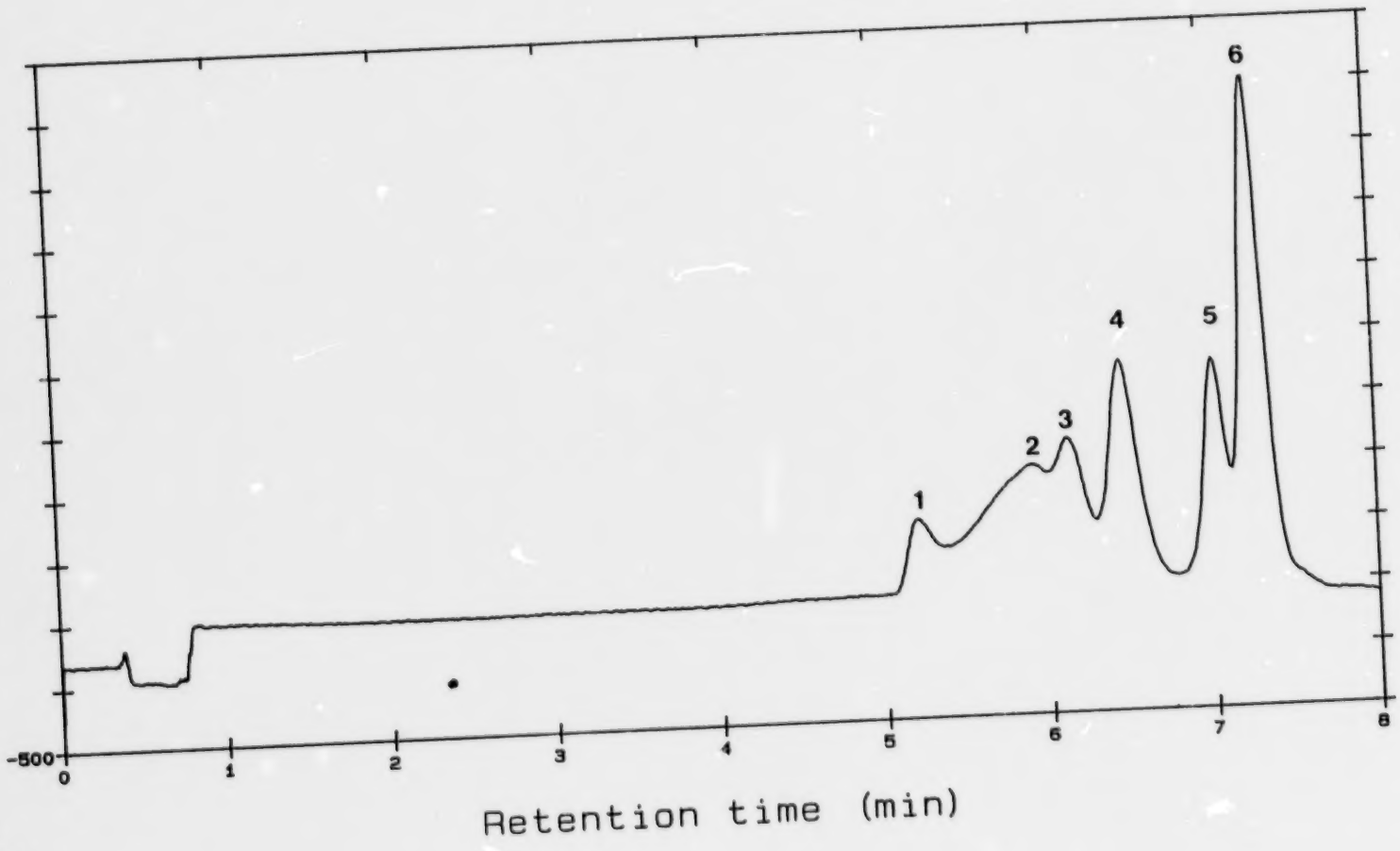


Figure 52: HPSEC separation of the extract of Narmco 5208 prepreg, batch #1014, heated 4 h at 100°C. Column: PLgel, 30 cm X 7.5 mm i.d..

6. RECOMMENDED METHODS FOR LIQUID CHROMATOGRAPHY

6.1 Preparation of acetophenone standard solution

(1) Weigh a stoppered 125 mL Erlenmeyer flask on an analytical balance.
(2) Add to the Erlenmeyer 0.5 mL of acetophenone.
(3) Weigh again to determine the weight of acetophenone.
(4) Add 50 mL of tetrahydrofuran.
(5) Weigh again to determine the weight of tetrahydrofuran.
(6) Calculate the concentration of acetophenone in THF (% by weight).
(7) Keep the flask tightly stoppered when not in use to prevent evaporation of THF.

6.2 Extraction of resin from the prepreg

(1) Weigh a 250 mL beaker on an analytical balance.
(2) Add to the beaker a piece of prepreg (5 cm x 5 cm).
(3) Weigh again to determine the weight of the prepreg.
(4) Weigh a stoppered 125 mL Erlenmeyer flask.
(5) Add 1 mL of the standard solution of acetophenone to the Erlenmeyer.
(6) Weigh again to determine the weight of solution and hence the weight of acetophenone.
(7) Extract the prepreg in three stages with 50, 30, and 20 mL of THF. After each stage (15 minutes), transfer the THF solution to the Erlenmeyer, being careful to ensure that all is transferred.
(8) Put the beaker and fibres in an oven at 120°C for one hour and cool in a desiccator.
(9) Weigh the beaker to determine the weight of the graphite fibres without resin, and thus, by subtraction, the weight of the extracted resin.

A typical experiment is described in the following lines:

Standard solution of acetophenone

Weight of Erlenmeyer (A) :	82.7909 g
Erlenmeyer + 0.5 mL of acetophenone (B) :	83.2753 g
Weight of acetophenone (B-A) :	0.4844 g
Erlenmeyer + acetophenone + 50 mL of THF (C) :	126.8852 g
Weight of THF (C-B) :	43.6099 g
%wt of acetophenone (100*(B-A)/(C-A) = D) :	1.0986%

Extraction:

Weight of beaker (E) :	106.8923 g
Beaker + prepreg (F) :	108.6795 g
Weight of prepreg (F - E = G) :	1.7872 g
Weight of Erlenmeyer (H) :	83.6535 g
Erlenmeyer + 1 mL of standard solution of acetophenone (J) :	84.5541 g
Weight of standard solution (J - H = K) :	0.9006 g
Weight of acetophenone ((D/100)*K = L) :	0.009894 g
Weight of beaker + dried graphite fibres (M) :	107.9308 g
Weight of graphite fibres (M - E = N) :	1.0385 g
Weight of extracted resin (G - N = P) :	0.7487 g
Prepreg resin content (100*P/G) :	41.89%

6.3 Experimental conditions for reverse-phase liquid chromatography

Column: C18 or C8 bonded phase. In this study, a MCH-5-n-CAP, 30 cm long x 4.0 mm i.d., was generally used. A Hypersil MOS-1 is also suitable. Both have 5 µm particles.

Injected volume: 5 µL (filtered).

Column temperature: 25°C.

Mobile phase flow rate: 1.0 mL/min.

Detector: UV at 230 nm.

Gradient: 50/50 ACN/H_2O to 100% ACN in 15 minutes (linear gradient), maintained for a further 15 minutes, then returned to the initial composition over a one-minute period. The column is equilibrated with the mobile phase for 25 minutes before injection.

The response of each peak (either area or height) is measured and normalized according to the formula:

$$\text{Normalized response} = \frac{\text{Response of peak}}{\text{Response of acetophenone}} \times \frac{\text{Wt. acetophenone (g)}}{\text{Wt. of resin (g)}} \times 100$$

It is recommended to inject the solution three times and to take the average of the normalized response. Ideally, it is preferable to perform three extractions to have a more representative value.

A simpler method may be used based on the ratios of the areas (or heights) of the major peaks with respect to that of TGDDM. In this case, acetophenone is not needed, nor is accurate weighing of the sample, unless it is necessary to determine the resin content of the prepreg.

Approximate retention times (in minutes) for the important peaks in Narmco 5208 (Figures 2 and 3):

Peak	MCH-5-n-CAP	Hypersil MOS-1
DDS	4.2	3.3
Acetophenone (ACP)	7.3	5.1
Reaction product (RP)	10.3	7.3
TGDDM	12.4	8.6
DGEBA	13.9	10.2

6.4 Experimental conditions for high-speed reverse-phase liquid chromatography

These are similar to those described in the previous section except for:

Column: Ultrafast C_{18}-3 (Varian), 4 cm long x 4.6 mm i.d., 3 μm particles.

Injected volume: 1 μL (filtered)

Flow rate: 2.0 mL/min

Gradient: 20/80 ACN/H_2O to 100% ACN in 3 minutes (linear gradient), maintained for a further 2 minutes, then returned to the initial composition within 0.1 minutes. The column is equilibrated with the mobile phase for 4 minutes before injection.

6.5 Experimental conditions for high-performance size-exclusion chromatography

Column: PLgel (Polymer Laboratories), 30 cm x 7.5 mm i.d., 5 μm particles

Eluent: THF

Flow rate: 1.0 mL/min.

Column temperature: 25°C.

Injected volume: 20 μL (filtered).

Detector: Refractive index or UV detector.

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